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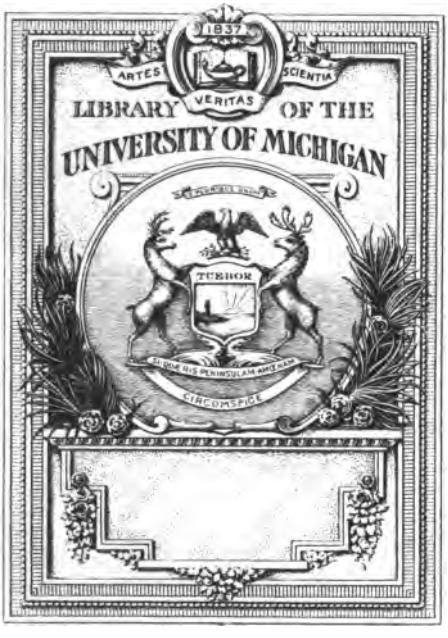
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IV.

ANALYSIS OF BABBITT

By

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the American Foundrymen's
Association.

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Copyright, 1919
By
JAMES BRAKES

©11-19-26 H.A.D.

Dedicated

to

my friend

FRANK L. NASON

Geologist
and
Mining Engineer.

PREFACE

IT is the desire of the author, to place before the mining, civil, electrical and mechanical engineer, and others, who have taken chemical analytical training, a small practical book on the analysis and manufacture of babbitt.

Many concerns would like to use, if possible, a babbitt made from a certain formula that has been known to give satisfaction in the past, and with care in weighing, selection of the furnace and observing certain precautions in melting the various metals, excellent results can be obtained with very little loss.

With the exception of the modification of the Alexander method for lead, the methods may be old, but they have been selected from the many methods in use for their simplicity, neatness and accuracy of analysis of a babbitt of known composition.

At the same time reactions and data have been inserted, which will be of interest to the student in analytical chemistry.

There is included, the titles of many methods by different chemists for the analysis of white metals and

white metal alloys, and also an extensive bibliography of books on metallurgical engineering.

To the young chemist, for whom this book has been especially written, it is the earnest desire that it may be of pleasure and profit.

I desire to publicly thank Dr. F. W. Schwartz for reading the manuscript and Miss Helen T. Gibney for reading the proofs.

JAMES BRAKES.

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INTRODUCTION

TO IZAAC BABBITT, to whom recognition is given as one that made a special study of bearing metal and was so successful in the art of making anti-friction alloys, that his name has been used to indicate the process as well as that of the alloy.

According to Buchanan, the original patent was issued for a particular form of bearing and not for a special anti-friction alloy.

The original was composed of 90 parts of tin and 10 parts of copper, later, it was said to be a mixture of tin, antimony and copper. A "hardening" is first prepared by melting 24 parts of tin, 8 parts of antimony and 4 parts copper. Each metal is melted separately, covered with powdered charcoal to prevent oxidation. The antimony is added to the tin after fusion and the copper after the molten alloy is removed from the furnace. This hardening, either in the form of ingots or direct from the furnace, is added to twice its weight of melted tin, the surface of which is covered with powdered coal and the resulting alloy is termed the lining metal, with a theoretical composition of tin 96 parts, antimony 8 parts and copper 4 parts, or tin 88.89%, antimony 7.41% and copper 3.70%.

The process of making the anti-friction alloy is again described as melting 4 parts of copper, add 8 parts of antimony, allow to cool to dull red heat, then add 16 parts of tin. This alloy is also termed "hardening" which is added to twice its weight of tin, the surface of the molten metal being covered as before with powdered coal.

Time has changed the formula and mode of manufacture of the above alloy, which at one time was extensively used, but it has been replaced in many cases by other alloys in which a portion of the tin has been substituted by lead and zinc, hence in recent years there are many anti-friction alloys on the market that are called babbitt, and the change of formula has been altered and influenced by the high price of tin and also by the general satisfaction that other alloys have given.

Each year the babbitt industry is becoming greater, and the alloys has been improved by the addition of a small percentage of certain metals (for which patents have been granted), which imparts a fine close and compact body to the alloy, thereby increasing its wearing and lasting qualities far greater than that of ordinary babbitt.

CHAPTER I.

ANTIMONY.

(Stibium.)

Said to have been discovered by Basil Valentine, a monk of Germany, in the fifteenth century. Schelenz[1] states that the name antimony comes from the Arabic. Wang Chung, *Yu*[2] has treated the subject of antimony in a thorough manner.

Properties, etc.—Chemical symbol, *Sb*; atomic weight, 120.2; trivalent usually; *Sp. Gr.* 6.713[3]; molten, 6.55 (631°C.)[4]; melting point, 632°C.[5]; volatilizes at about 1500°C. Specific heat at about melting point, .054[6]; latent heat of fusion, (calculated) 16.0 Cal.[7]; increase in volume on melting, 1.4%[8]; electrical conductivity (Ag=100) 4.6[9]; casting temperature 710°-1050°C.[10]; Foliated, crystalline scale like structure; silver white-color when pure, but the commercial has a bluish-white tint; strong metallic lustre; very brittle and easily reduced to powder; neither ductile or malleable; not readily acted upon by the air; tarnishs slowly in warm moist air; burns with a blueish white light when heated to redness in the air; alloys particularly with the

[1] *Antimony. Schelenz. Z. Angew. Chem.*, 26, 1311-2.
[2] *Antimony. Wang Chung Yu. (f).*
[3] *Long.*
[4] *Pascal and Joumiaux.*
[5] *Pouillet.*
[6] *Hofman.*
[7] *Richards.*
[8] *Toeplar.*
[9] *Matthiessen.*
[10] *Wust.*

metals, *Pb*, *Bi*, *Sn*, *Cu*, *Ni* and *Fe*. Used technically in the manufacture of alloys (Britannia metal, hard lead, white metal, bearing metal); imparting hardness and expansion to alloys when cooling from the molten state; manufacture of thermoelectric piles, blacking iron, coating metals, antimony black; is employed to impart a metallic surface to plaster casts and to cast zinc ornaments; alloy for printing type; preparation of tartar emetic and other pharmaceutical products; the metal is at present rarely used medicinally, but at one time was used for leprosy; the slow cooling of the commercial metal produces a peculiar coarse laminated, crystalline, rhombohedra structure required in commerce, which is regarded as the best star-antimony, whereas, if cooled quickly, the fracture is granular. Native antimony usually contains *Ag*, *Fe* and *As*, with a specific gravity of 6.5–7. In combination with other ores, but the chief ore is stibnite, Sb_2S_3. A high fusion point is a sign of its impurity; pure metal is usually prepared by the Liebig process[1]; important in the refining of argentiferous lead; dissolves slowly in hot HCl; converted to the pentoxide by HNO_3; H_2SO_4 first oxidizes it and then converts it to the sulphate; soluble in cold aqua regia, and the solution contains $SbCl_3$ or $SbCl_5$, depending upon the concentration of the acid and the time of action; antimony pigments as a substitute for white lead and zinc paint, being innocuous, permanent and sun proof; the use of the sulphide in the rubber industry. Commercial antimony (98.46% *Sb.*) *Sp. Gr.* 6.69. 1 cubic foot weighs 417.6 pounds. Immense quantities of *Sb* compounds are used in wall paper, textile fabrics, paper dyeing and printing. No clearly defined case of antimonial poison-

[1]*Rosc. and Schorm. Vol. II, Pt. II,* 304.

ing has been established,[1] but opinion differs as to the poisonous action of *Sb* on workmen. A very small percentage of *Sb* in *Cu* lowers its conductivity. According to Hiorns and Lamb, the effect of *Sb* on the conductivity of *Cu* is indicated by the following figures .000% *Sb*, 100; .098%, 76; .203%, 70; .208%, 68.5; .392%, 58.4; .461%, 48.9; .605%, 42.4; patents have been granted for the manufacture of finely divided *Sb* by electrolysis, for medicinal uses. Schrumpt and Zabel state that typesetters suffer from a general debility and that the complaint was traced to *Sb* poisoning. According to Poppe and Polenski, *Sb* added to barley flour, used for fattening geese, does not produce an abnormally fat liver as generally believed. Flour containing no *Sb* seems to produce the same results. Seltzer and carbonated waters have an action upon the alloys of *Sn*, *Sn-Pb* or *Sn-Sb*, used for stopping the siphons. The action is assisted by electrolytic action; antimony has been found in foods that have been prepared in enameled cooking utensils. Chinese "crude" *Sb* contains Sb_2O_3 and metallic *Sb*. (Schoeller). Kahlbaum's "technical" *Sb* contains as impurities *Cu*, *Pb*, *Fe*, *Ni*, *Co*, *Sn* and *As* (impurity= $1:10^2$), and Kahlbaum's "pure" *Sb* is of higher purity, but the ratio of the impurities to *Sb* has not been established. (Mylius). According to Guettier the specific gravity of *Sb-Sn* alloys is below that of the calculated specific gravity of the mixture. The best alloys of *Sb* and *Sn* are made by having nearly the proportion of *Sb* 20 parts and *Sn* 80 parts, casting at a low temperature and using cold molds to prevent segregation of *Sb*.

[1]*Textil Faerb.-Ztg.*, 8, 39, *also Loewenthal. Chem. Ztg.*, 33, 1325.

Hardness (talc=1), 3.3[1]; coefficient of linear expansion per degree *C.* ($O°$-$100°$) .0000168[2]; normal to axis, .0000089[2]; tensile strength at ordinary temperature (pounds per square inch) cast, 1,000; specific heat for $t°C.$, *Sm* (*o* to *t*) $.04864+.0000084t^3$; specific heat at about 15°C., .048[2]; at 1°-20°, .0503; at 632°-830°C., .0603. Boiling point, visible ebullition, 1420°C.[4]; Young's Modulus[5] $(E)=7.8 \times 10^{11}$; modulus of rigidity [5]$(\mu)=2 \times 10^{11}$.

Metallurgical processes. (1) liquation process; (2) Crucible process; (3) open-hearth process; (4) English process; (5) volatilization process; (6) French process; (7) electrolysis; (8) elec. furnace process.

The process used, depends upon the locality, cost of production, market price and demand for the metal.

Natural Sources:

Native Antimony, (Sb) rare; STIBNITE, (Sb_2S_3); valentinite, (Sb_2O_3); senarmontite, (Sb_2O_3); cervantite, (Sb_2O_4); stiblithe, $(Sb_2O_4+H_2O)$; kermesite, $(2Sb_2S_3\ Sb_2O_3)$; also waste product from smelting ores as pyrargyrite, $(Ag_6Sb_2S_6)$; berthierite, $(FeSb_2S_4)$; freieslebenite, $(Ag_{10}Sb_2S_8)$; wolfsbergite, $(Cu_2Sb_2S_4)$; bournanite, $((Cu_2Pb)_3Sb_2S_6)$; boulangerite, $(PbSb_2S_4)$; bleinierite, $(Pb_2Sb_2S_5)$; dyscrasite, (Ag_2Sb); ullmannite, $((NiSSbAs)_2)$; breithauptite, $(NiSb)$; allemontite, (As_3Sb_2).

Mining Localities:

Andreasberg in the Harz; Przibram in Bohemia; Sahl in Sweden; Sarawak in Borneo; Constantine in Turkey; Tuscany in Italy; Algeria, Canada, Mexico, France, United States, Chili, Japan, China, Nova Scotia and New South Wales.

[1]*Mohs.* [2]*Hofman.* [3]*Naccaria.* [4]*Greenwood.* [5]*Bridgman.*

References:

Antimony. Wang. (*f*).

The Antimony Industry. Howard. (*g*).

Production of Antimony in the United States.[1]

The production of antimony ore in the United States in 1916 amounted to about 4,470 short tons, carrying about 1,770 short tons of antimony. Alaska produced during the year of 1917, antimony valued at $40,000.

Production of Antimony in the United States.[2]

Antimony in antimonial lead in 1914 was 3,535 tons. Antimony from domestic ores in 1915 was about 2,100 tons. This does not include the production of antimony in antimonial lead which was 3,288 tons. The production of 1916 was much smaller owing to the rapid decline of antimony prices.

Commercial Metals.[3]

Analysis of some of the more important brands of antimony:

Cookson's—*Sb* (by difference), 99.874; *Pb*, .041; *Sn*, .035; *As*, *tr.*; *Cu*, .04; *Fe*, .010; *Zn*, *tr.* Cookson's—*Sb* (by difference, 99.608; *Pb*, .102; *Sn*, *tr.*; *As*, .092; *Bi*, none; *Cu*, .046; *Cd*, none; *Fe*, .004; *Zn*, .034; *Ni* and *Co*, .028; *S*, .086. Hallett's—*Sb* (by difference), 99.104; *Pb*, .669; *Sn*, .175; *As*, *tr.*; *Cu*, .038; *Fe*, .014; *Zn*, *tr.* Hallett's—*Sb* (by difference), 99.045; *Pb*, .718; *Sn*, .012; *As*, .021; *Bi*, none; *Cu*, .046; *Cd*, none; *Fe*, .007; *Zn*, .023; *Ni* and *Co*, none; *S*, .128. Japanese—*Sb* (by difference), 99.325; *Pb*, .443; *Sn*, .175; *As*, .008; *Cu*, .034; *Fe*, .015; *Zn*, *tr.* Japanese—*Sb*, 99.195; *Pb*, .424; *Sn*, .012; *As*, .095; *Bi*, none; *Cu*, .043; *Cd*, none; *Fe*,

[1] *U. S. Geol. Survey (communication).*
[2] *Met. and Chem. Eng. (communication).*
[3] *Min. and Sci. Press, July* 10, 1915.

.007; *Zn*, .023; *Ni* and *Co*, none; *S*, .201. Chinese—*Sb* (by difference), 99.915; *Pb*, .018; *Sn*, .035; *As*, .017; *Cu*, .008; *Fe*, .007; *Zn*, *tr.* Chinese—*Sb*, 99.760; *Pb*, .029; *Sn*, none; *As*, .090; *Cd*, none; *Fe*, .004; *Zn*, .027; *Ni* and *Co*, *tr.*; *S*, .078.

Qualitative Analysis.

Dissolve .2-.3 gram of the powdered metal in 2 or 3 *c. c.* of hot aqua regia, add 20 *c. c.* of water and about 1 gram of $Na_2SO_3+7\ H_2O$. Heat nearly to boiling, and when the odor of SO_2 is perceptible, pour the solution into about 300 *c. c.* of cold water. If *Sb* is present, a white bulky precipitate of ANTIMONIOUS OXYCHLORIDE (powder of Algaroth), will be precipitated.

$$4\ SbCl_3+5\ H_2O=2\ (Sb\ O\ Cl)\ Sb_2O_3+10\ HCl.$$

Precipitate soluble in $H_2(C_4H_4O_6)$ and water, reprecipitated by H_2S as Sb_2S_3, orange-red precipitate. (*Bi O Cl* under similar conditions, will become black Bi_2S_3).

Dissolve .1-.2 gram of the powdered metal, in 1 or 2 *c. c.* of aqua regia, and evaporate to dryness. Add 1-2 *c. c.* of *HCl* and about 10 *c. c.* of water and heat until solution is clear. Place a piece of metallic *Zn*, supported on platinum foil in the solution and allow to stand a few minutes, remove the black stained foil, place in small beaker and add 2 drops of HNO_3, $H_2(C_4H_4O_6)$ and water, and heat to dissolve. Filter, if necessary, and add H_2S to the filtrate; an orange-red precipitate of Sb_2S_3 indicates *Sb*.

Heat with the blow-pipe on charcoal, a small fragment of the metal and condense the copious white fumes on cold procelain. Place 1 or 2 drops of $(NH_4)_2S$ in contact with the white sublimate; an orange-red coloration indicates *Sb*, due to the change of the volatile Sb_2O_3 to Sb_2S_3.

Dry on a filter, a portion of the white precipitate obtained by the addition of water. Moisten with a few drops of $(NH_4)_2S$; an orange stain indicates Sb_2S_3; a black color denotes Bi_2S_3.

H_2S precipitates all the Sb from moderately acid antimonious solutions as Sb_2S_3; imperfectly from alkaline and neutral solutions.

Sb_2S_3 is insoluble in $(NH_4)_2CO_3$ and dilute acids; soluble in concentrated HCl with evolution of H_2S; soluble in KHO and alkaline sulphides containing an excess of S.

H_2S precipitates Sb_2S_5, mixed with Sb_2S_3 and free S from HCl solutions of antimonic acid. Soluble in boiling HCl, hot $NaHO$ and NH_4HO; soluble in $(NH_4)_2S$, from which solution it is reprecipitated by HCl.

Quantitative Analysis.

$K_2Mn_2O_8$ Method.

Volumetric Method.—Place .5 gram of the finely divided alloy in a dry 400 *c. c.* beaker. Add 10 *c. c.* of strong H_2SO_4, cover and heat until the alloy is entirely decomposed (about 10 or 15 minutes). Cool, add 150 *c. c.* of water, 15 *c. c.* of strong HCl and boil 5 minutes. Cool and titrate rapidly with standard $K_2Mn_2O_8$ solution to a rose color. Subtract blank and calculate Sb. (titration must be rapid and the first coloration taken).

$$K_2Mn_2O_8+5\ SbCl_3+16\ HCl= 5\ SbCl_5+\ 2\ HCl+2\ MnCl_2+8\ H_2O$$

$$K_2Mn_2O_8=10\ Fe=5\ Sb. \quad Sb=2\ Fe=\frac{120.2}{111.68}=$$

1.0763, and therefore multiply the Fe factor by 1.0763 and the product will equal the Sb factor.

Standard $K_2Mn_2O_8$ Solution.[1]

[1]*This solution is also used for Fe, P, Mn, Ti and CaO.*

Dissolve 3.70 grams of $K_2Mn_2O_8$ *c. p.*, in 1000 *c. c.* of water and standardize as follows:

Dissolve 1.4 grams of $FeSO_4(NH_4)_2SO_4+6\ H_2O$ (14.24% *Fe.* Merck, blue label), in a cold mixture of 150 *c. c.* of water+10 *c. c.* of H_2SO_4, titrate to a rose color and subtract blank.

$$1\ c.\ c. = \frac{1.4 \text{ grams } FeSO_4(NH_4)_2SO_4 + 6\ H_2O \times .1424}{31.\ c.\ c. - .1\ c.\ c.\ K_2Mn_2O_8 \text{ solution}}$$

=.006451 gram of *Fe*, and .006451 × 1.0763= .006943 gram of *Sb*.

No. 2 Babbitt.

$$\frac{.006943 \times 12.8\ c.\ c. - .1\ c.\ c.\ K_2Mn_2O \text{ solution}}{.5 \text{ gram of alloy}} \times 100 = 17.63\%\ Sb.$$

Mixture calculation=18.00% *Sb* and, as the commercial metal contained 98.46%, the actual content was 17.72% *Sb*.

Determination of Sb in Commercial Metal.

Weigh .5 gram and treat as usual, until the final solution obtained is ready for titration. Transfer solution to a 250 *c. c.* marked flask, dilute to the mark and mix thoroughly. (1 *c. c.* of solution contains .002 gram of metal). Take 100 *c. c.* of the solution with pipette and place in 400 *c. c.* beaker. Add 10 *c. c.* *HCl* and titrate the cold solution with standard $K_2Mn_2O_8$. Subtract blank and calculate *Sb*. Accuracy of method, 98.38%-98.55% *Sb*.

The $K_2Mn_2O_8$ solution can be standardized with $KSbC_4H_4O_7 \cdot \frac{1}{2}H_2O$[1], *C. P.* From the formula, it should contain 36.16% *Sb*. The *Sb* must be determined in the salt, before it can be used as a standardizing reagent and this can be done very accurately by the following method.

Place .5 gram of the pure salt in 400 *c. c.* beaker and dissolve in 10 *c .c.* of hot water. Add 15 *c. c.* of strong *HCl* and 100 *c. c.* of water. Cool and titrate as usual, with standard $K_2Mn_2O_8$ solution. Multiply the *Fe* factor by 1.0763 and the product will equal the *Sb* factor.

$$A = \frac{.006764 \times 27.7 \text{ c. c.} - .1 \text{ c. c. } K_2Mn_2O_8 \text{ solution}}{.5 \text{ gram}} \times 100 = 37.33\% \ Sb.$$

$$B = \frac{.006764 \times 27.7 \text{ c. c.} - .1 \text{ c. c. } K_2Mn_2O_8 \text{ solution}}{.5 \text{ gram}} \times 100 = 37.33\% \ Sb.$$

The salt is permanent, as the results from the above sample gave ten years later, the following results.

$$C = \frac{.006904 \times 27.1 \text{ c. c.} - .1 \text{ c. c. } K_2Mn_2O_8 \text{ solution}}{.5 \text{ gram}} \times 100 = 37.28\% \ Sb.$$

N/10 $K_2Mn_2O_8$ Solution.

Dissolve 3.16 grams of $K_2Mn_2O_8$ *C. P.* in 1 liter of water. 1 *c. c.*=.005584 gram of *Fe* (theoretical), and $K_2Mn_2O_8$=10 *Fe*, also *Sb*=2 *Fe* then
111.68 : 120.2=.005584 : X. X=.00601 gram of *Sb*. (theoretical).

$KBrO_3$ Method.

[1]*It is said that a small portion of the Sb in tartar emetic is present as antimonic salt. (Coblentz and May. Merck's Report* 18, 195.)

Volumetric Method.—Place .5 gram of the finely divided alloy in a 400 *c. c.* beaker. Add 20 *c. c.* of HCl and a few drops of bromine. Shake frequently and warm gently until dissolved. Dilute to 75 *c. c.* with water and boil until free from Br (about 8 minutes). Dilute with water to 125 *c. c.* Add 1 gram of $Na_2SO_3 . 7H_2O$ and boil down to 75 *c. c.* Wash cover and sides of beaker with water, add 10 *c. c.* HCl and heat to boiling. Add 3 drops of methyl orange solution (.05 gram of the salt dissolved in 15 *c. c.* of water) and titrate with standard $KBrO_3$ until the solution is colorless.

$N/10$ $KBrO_3$ Solution.

Dissolve 2.7836 grams of pure $KBrO_3$ in 1000 *c. c.* of water.

$$2\ KBrO_3 + 2\ HCl + 3\ Sb_2O_3 = 2\ KCl + 2\ HBr + 3\ Sb_2O_5$$

$2\ KBrO_3 = 6\ Sb$

$2\ KBrO_3 = 167.02 \times 2 = 334.04$

$6\ Sb \quad = 120.2 \times 6 = 721.2$

$334.04 : 721.2 = 2.7836 : X \qquad X = 6.01$

1000 *c. c.* $N/10$ $KBrO_3$ *V. S.* containing 2.7836 grams $KBrO_3$=6.01 grams Sb.

1 *c. c.* $N/10$ $KBrO_3$ *V. S.* containing .0027836 gram $KBrO_3$=.00601 gram Sb. (theoretical.)

Standardize the $KBrO_3$ solution as follows: Place .5 gram of $KSbC_4H_4O_7 . \frac{1}{2} H_2O$, *C. P.* in 400 *c. c.* beaker and dissolve in 10 *c. c.* of hot water. Add 30 *c. c.* HCl, dilute to 75 *c. c.* with water and heat to boiling. Add 3 drops of methyl orange solution and titrate with $KBrO_3$ solution.

$$1\ c.\ c. = \frac{.3733 \times .5 \text{ gram } KSbC_4H_4O_7 . \frac{1}{2} H_2O}{31.15\ c.\ c.} = .005992 \text{ gram } Sb.$$

No. 2 Babbitt.

$$\frac{.005992 \times 14.9 \text{ c. c. } KBrO_3 \text{ solution}}{.5 \text{ gram of alloy}} \times 100 = 17.85\% \ Sb.$$

Electrolytic Method.—Place .5–1 gram of the finely divided alloy in 150 *c. c.* beaker and warm gently with a mixture of 4 grams of $H_2C_4H_4O_6$+4 *c. c.* of $HNO_3(1.42)$+15 *c. c.* of water, heat and shake until solution is complete. Add 4 *c. c.* of $H_2SO_4(1.84)$, dilute with 20 *c. c.* of cold water and transfer to a 250 *c. c.* marked flask. Cool, dilute to the mark, mix and allow to settle. Take 50 *c. c.* with pipette, place in 250 *c. c.* beaker and neutralize with a concentrated solution of $NaHO$. Add 2 grams in excess and heat gently to obtain a clear solution. Add 50 *c. c.* of a saturated solution of $Na_2S(1.20)$, heat to boiling and allow to settle. Filter and wash with 30 *c. c.* Na_2S solution (1.20) diluted with water. The solution should now contain 80 *c. c.* of saturated solution of Na_2S and 2 grams of $NaHO$. Evaporate or dilute to 125 *c. c.*, add 25 *c. c.* of alkaline solution of $H_2O_2(3\%)$ and heat the solution until it is nearly colorless. Electrolyze with a current of ND_{100}= 1.5–1.6 amperes and 2.1–1.45 volts. Time 2.5 to 6 hours. When the Sb is all deposited, wash the cathode with distilled water without interrupting the current, by lowering the beaker and directing a fine spray of water over the surface of the cathode, and then immerse in C_2H_6O for a few seconds. Dry in air bath for 15 minutes at a temperature of 80°–90°C. Cool and weigh.

Weight taken=.5 gram and solution diluted to 250 *c. c.*

then 50 *c. c.*=.1 gram $\left(\frac{.5 \text{ gram}}{250 \text{ c. c.}} \times 50 = .1\right)$.

The area of the electrode cylinder of platinum gauze=

6.3 sq. in.=40.6 sq. cm. and $\frac{1.6 \text{ amperes}}{.406}$=4 amperes.

Used 4 amperes—3.1 volts. (four 32 *c. p.* carbon lamps in parallel.) Time 2.5 hours.

(1) Cylinder+deposit=10.0505 grams.
" =10.0414 "

$$\frac{.0091 \text{ gram.}}{.1 \text{ gram alloy.}} \times 100 = 9.10\% \ \textbf{\textit{Sb.}}$$

(2) Cylinder+deposit=10.0504 grams.
" =10.0412 "

$$\frac{.0092 \text{ gram.}}{.1 \text{ gram alloy.}} \times 100 = 9.20\% \ \textbf{\textit{Sb.}}$$

(3) $K_2Mn_2O_8$ Method=9.13% *Sb.*

According to Classen, "the following equations probably represent the reactions which take place in the electrolysis of the antimony sulpho-salt."

At the cathode:

$$Sb_2S_3+3\ Na_2S+6\ H=2\ Sb+6\ NaHS.$$

At the anode:

$$6\ NaHS+3\ O=3\ Na_2S_2+3\ H_2O.$$

After the cathode and the deposit of antimony has been weighed, place it in a solution of dilute HNO_3(1:1) and allow to stand about 1 hour. Should the above

solution fail to remove the deposit, fill a 50 *c. c.* platinum crucible with $HKSO_4$ within ¼ inch of the top. Fuse, place cathode in the melted salt and allow to remain 3 to 5 minutes. Remove, cool and place in warm water containing HCl and, after the salt has dissolved, wash thoroughly with water. Dry and the cathode is ready for use.

To determine the end of the electrolytic reaction, place a bright piece of platinum foil in contact with the cathode. Should there be a deposit, redissolve it by placing the foil in contact with the anode.

Sodium Sulphide Solution.

Dissolve 85 grams of $NaHO$ in 200 *c. c.* of water (*Sp. Gr.* of solution=1.3). Divide the solution into two parts and pass H_2S through one part, free from air, until the odor of H_2S in solution is decided. Filter, add the remaining part and pass H_2S until the solution is saturated. Filter through cotton, cork tightly and set aside in cool dark place.[1]

In passing H_2S through the colorless solution of $NaHO$, the color becomes in succession, yellow, orange, brown and finally, a straw color when the solution is saturated with H_2S. The volume increases from 200 *c. c.* to 290 *c. c. Sp. Gr.* 1.20. Time 12 to 15 hours for the absorption of H_2S.

$$\begin{array}{l} 2\ NaHO + H_2S = Na_2S + 2\ H_2O \\ \quad\ \ 80 + 34\ \ = 78\ \ \ + 36 \end{array}$$

$$\begin{array}{ll} 80:78=85:X & X=82.8 \text{ grams } Na_2S \\ 34:78=X:82.8 & X=36.1 \text{ grams } H_2S \end{array}$$

[1]*If the monosulphide is required, saturate one half of the NaHO solution with H_2S, add the other half and filter directly into stoppered bottles.*

$$\frac{36.1 \text{ grams.}}{1.53 \text{ grams.}} = 23.6 \text{ liters of } H_2S,$$

at $0°C.$ and 760 *m. m.* of *Hg.*

Saturated solution of Na_2S made from the salt.

At 10°C—1.15 *Sp. Gr.*
" 25°C—1.20 " "
" 32°C—1.20 " "
" 38°C—1.225 " "

To prepare the Na_2S solution for the separation of *Sn* and *Sb* from the other metals, dissolve the colorless *c. p.* salt in water as needed. Saturate with washed H_2S, allow to settle, filter, bottle, cork tightly and keep in cool dark place.

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CHAPTER II.

TIN.

(Stannum.)

The metal has been known from the most remote antiquity. The county of Cornwall, has yielded tin for at least 3,000 years and the mines of Cornwall, have been worked for the oxide of tin since the time of the Phoenicians and Greeks.

The alchemistic name for this metal was *Jove*, and was indicated by the sign of Jupiter.

Properties, Etc.:

Chemical symbol, *Sn*; atomic weight, 118.7; quadrivalent; *sp. gr.*, 7.28 (pure); hammered, 7.29; cast, 7.29; rolled, 7.30; electrolytic, 7.25; rhombic, 6.55; molten, 6.98 (232°C.)[1]; melting point, 232.7°C.[2]; volatilizes preceptible at 1200°C. Boiling point, 1550°C.[3] (approximate). Specific heat at about melting point, .059[4]; latent heat of fusion, 13.7 Cal,[5] (calculated); heat conductivity (*Ag*=100) 14.5; increase in volume on melting 2.8%[6]; electrical conductivity (*Ag*=100) 13.1[7]; casting temperature 500°C.[8] Crystalline structure; color, silver-white with a slight bluish tinge; brilliant lustre, not easily tarnished; soft, very malleable and laminable,

[1]*Pascal and Joumiaux.*
[2]*Person.*
[3]*Carnelly.*
[4]*Hofman.*
[5]*Richards.*
[6]*Toeplar.*
[7]*Matthiessen.*
[8]*Hofman.*

but not very ductile and with feeble tencity. Rolled to sheets not over 1/5000 of an inch thick; most malleable at 100°C.; most brittle at 200°C.; when rubbed gives a peculiar odor similar to that of $SnCl_2$ solutions. The temperature of the metal when cast, determines entirely its lustre, and degree of cohesion when cold; rarely used in the pure state for casting as it does not fill the molds entirely. If the metal is poured too hot (exhibiting rainbow colors on the surface), the metal will be brittle, if again heated to 100°-140°C. If the temperature is too low when poured, the metal will be after cooling, dull and brittle. To obtain the best results as to metallic lustre and at the same time the greatest cohesive strength, the metal must be cast when the surface of the molten metal presents a high degree of lustre. Tin-ash is a mixture of *SnO* and finely divided *Sn*, formed by allowing the fused metal to stand in contact with air, and if the heating is continued, the greyish coating is converted to yellowish-white SnO_2, known as putty powder; resists the action of organic acids to a remarkable degree; next to *Pb*, it is the softest metal; a bar of tin when bent gives a peculiar creaking sound (cry of tin), caused by the grinding action of the crystals over each other.[1] Alloys of *Sn* 90% and *Pb* 10% preserve the crackling sound, but in a less degree to that of pure tin, and the sound is destroyed by the addition of 1% of *Zn*. Tin pest, a breaking down of the structure of the metal, to a grey friable powder by extreme cold. The action is said to begin at 18°C., and is most rapid at —48°C. Some writers state that the tin pest is a disease of tin, as normal tin is affected when placed in contact with the grey powder. (the author has exposed granulated and bar tin at a temperature of 18°C., to —41°C., the

[1]*Or the breaking up of crystals along cleavage planes.*

entire winter, with no perceptible change in the structure. No doubt, the structure of the metal becomes very brittle by extreme cold (which acts upon the metal like extreme heat), and when the pigs of tin are piled, the weight of the pigs above, may crush the lower tier to irregular fragments and also to a powder.). The affinity of the oxides *Sn* and *Pb* for each other, is shown by heating to a red heat, an alloy of 1 part of *Sn*+4 parts of *Pb*. Combustion begins similar to that of burning peat or charcoal, and is continued for some time after the heat is removed by using a gentle blast. At ordinary temperature, the polished surface of tin-plate is but little affected by the air or moisture, but the bright surface of commercial metal soon tarnishes under the same conditions. Commercial metal often contains small portions of *Fe*, *Pb*, *Cu*, *Sb*, *As*, *Bi*, *W*, and in some cases, *Mn* and *Zn*. The alloys of tin are very valuable. Britannia metal, speculum-metal, gun-metal, bell-metal, pewter, hard and soft solder, engineering alloys, composition and anti-friction alloys, fusible alloys, bronze, phosphor-bronze, and tin amalgam. Tin-plate is thin sheet iron coated with tin. Tin-foil is made from the pure metal or alloyed with *Pb*, and is extensively used as a covering or packing for perishable and deliquescent material. The crystalline appearance given to sheet tin (*Moire Metallique*), is obtained by rinsing the clean tin plates in dilute HNO_3 or $HCl+HNO_3$ and then with water. The plates are now dipped for a few moments in aqua regia, diluted with 3 volumes of water and heated to about 180°F. The plates are now removed, washed thoroughly with water, dried, and finally oiled or lacquered. The pure metal is used largely for block tin worms for distilling apparatus, block tin pipes for gas and water, working parts of certain dry and wet gas meters, tin

plated ware for household and pharmaceutical use and the tinning of lead, copper and other metals. The metal has the remarkable property of imparting hardness to certain alloys, which was known to the alchemists, who applied the term of *diabolus metallorum* to some of its brittle alloys. Tin conbines with lead in all proportions and strongest alloy of the two metals, is said to be 3 parts of Sn+1 part of Pb. *sp. gr.* 8. Sn and Cu do not unite readily with each other, and the resulting brittle alloys, is less brittle and more malleable, if heated and then plunged in cold water. Tin and zinc, when fused, unite readily to form alloys. As the Zn predominates, the metal must be cooled quickly, otherwise the metals may separate at the bottom of the molds. The addition of Pb to the above alloys, increases the body of the alloy. Sn and Sb form white brittle alloys, the brittleness increases as the percentage of Sb becomes greater and the alloys must solidify quickly to prevent segregation. According to Chaudet, 10 parts of Sn to 1 part of Sb, form a perfectly ductile alloy. The elasticity, hardness and toughness of ordinary bronze, is greatly increased by the addition of .25 to 2.5% of P, the alloy is now known as phosphor-bronze. $SnCl_2+2\ H_2O$ is a powerful deoxidizing reagent, as it reduces the salts of Hg, Ag, Pt, etc., to the metallic state and the solutions of other metals from the *ic* to the *ous* condition. Pure stannous chloride ($SnCl_2+2\ H_2O$), is used as a mordant by dyers and calico printers, also for preparation of fuchsine. Stannic chloride ($SnCl_4+5\ H_2O$) and stannate of sodium (Na_2SnO_3), are valuable salts of the dyer. Phosphor-tin is a valuable alloy. When the borings (5% P) are treated with acid, there is an evolution of H_3P which ignites in contact with the air. The protoxide (SnO) acts as a base, and the peroxide (SnO_2) as a basic and

an acid forming oxide. The prepared peroxide is used for polishing glass and stone and is known as putty powder. After ignition, pure SnO_2 is an amorphous white or straw colored powder. SnO is a grayish black color usually, and when pure according to Roth, a red color. The sesquioxide, Sn_2O_3 is gray. SnO_2 forms two hydrates, both acids: stannic acid, SnO_2, H_2O, and metastannic acid, Sn_5O_{10}, 5 H_2O. The commercial metal consists of common, refined and grain. Refined tin is made from the purest ores and grain tin from the best pigs. Tin wire has but slight tenacity. Arsenic renders the metal whiter, but harder and the presence of small amounts of *Pb*, *Cu* and *Fe* causes it to become brittle. When $SnCl_4$ is mixed with one-third of its weight of water, it is termed *butter of tin.* Powder of tin was used exclusively as an anthelmintic, and is now used as a teniafuge. The medicinal preparations are still called *jovial* preparations. The metal is soluble in HCl with the evolution of H; hot HNO_3 converts it to insoluble metastannic acid; soluble in hot H_2SO_4 and aqua regia. Native tin has been found in small tablets in bismutite from Mexico. Commercial tin (99.70% *Sn*) *Sp. Gr.* 7.33. 1 cubic foot weighs 457.57 pounds. Shrinkage of castings per foot 1/12 or .0833 of an inch. Wire made from iron, 7/100 of an inch in diameter, will sustain 444 pounds, and tin wire if the same size, 32 pounds. "Strain disease," caused not only by a rise in temperature but also by contact of one article with another already affected. Affection taking place at a temperature as high as 37°C. "Museum disease," coins, medals, organ pipes and utensils made from tin, become covered with wart-like spots of a grayish color, changing to a grayish dust. Cavities are left, which become enlarged and increase in size. Said to be a change from white to

gray tin. Tin that has been distilled in *vacuo*, has a brass-yellow color due to the presence of a little sulphur. Portuguese counterfeit money contained as the principal component 90.8–98.3% *Sn* in most of the coins. The size of the crystal grains in bar tin, determine the intensity of the "cry of tin." Alloys containing free *Sn*, free *Bi* and free *Sb*, will also give the sound, only in a lesser degree. Qual. analy. of tin ash show *Sn*, SnO_2, *Sb* trace, *Cu*, *Fe*, *C* and SiO_2. The samples are not homogeneous. As high at 50.6% *Pb* has been found in tin coatings used for wrappings. Chocolates containing acid substances that have been wrapped in zinc foil, that has been used as a substitute for tin foil, varied in content from 141 to 287 *mg.* of zinc oxide per *kg.* Opinions differ as to the weight of tin dissolved by decoctions of coffee. According to the Municipal Lab. of Leipzig, two samples of filtered coffee yielded 7.8 and 8.8 *mg.* of tin resp. Strunk was unable to verify these findings in any particular. The amount of tin found in unvarnished cans of spinach, at least one year old, was less than 126 *mg.* per *kg.* The tin content was always lower in the varnished cans. Canned spinach containing 18 *mg.* of tin originally, after remaining open six days, 1038 *mg.* of tin were present. The amount of tin in the liquor increases with the length of time in storage. Samples of canned goods 5–8 years old contaminated with solder, amounts of tin has been found from traces to 3000 *mg.* per *kg.* Preserved asparagus which is said to have caused poisoning, contained .29 gram of tin per *kg.*, bound in the vegetable. Staphylococcus infections have been treated with a mixture of *Sn* and *SnO*, and a 5 to 10 per 1000 solution of $SnCl_2$ in water or glycerol was used for dressing war wounds; it is said in some localities that tin-platers never have

feruncles. Fusible tin boiler plugs are rendered dangerous by the formation of SnO_2, either as a solid mass at the fire end of the plug or throughout the tin filling. The presence of .3% *Zn* and a small amount of *Pb* is said to cause oxidation of the filling. The cooling curves of the freezing point of *Sn* detects the presence of *Pb* or *Zn* in the plugs as low as .1%. The addition of *Sn* to *Cu*, lowers the ductility, electrical conductivity and specific gravity, and increases the strength and hardness. Specific heat at about 15°C., .055[1]; at 19°-99°C., .0552; at 240°C., .064. Boiling point, visible ebullition 2275°C.[2] volatilization commences, 880°C.[3] Hardness (talc=1) 2.0-3.0[4]; coefficient of linear expansion per degree C. ($O°$-100°), .0000227[1]; tensile strength at ordinary temperature (pounds per square inch) cast, 4,600; drawn, 5,800; coefficient of rigidity,[5] 2.04×10^{11}; Bulk Modulus,[5] 5.29×10^{11}; Young's Modulus,[5] 5.43×10^{11}; specific heat for t°C., *Sm* (o to t) $.0560 + .000044t$.[6]

Metallurgical Processes:

(1) Blast furnace process, which is the oldest known method of smelting tin and is used for pure coarse lump ore and poor slags; (2) reverberatory furnace process, for reducing fine and low grade ores and rich slags; (3) electric furnace process is usually used for roasted ores; (4) electrolytic solution and deposition, used for the recovery of tin from tin plate waste and old scrap.

Natural Sources:

CASSITERITE (SnO_2). Varieties, lode tin, tin stone, wood tin, float tin and stream tin. It is the commercial ore of tin; stannite ($(CuSnFe)S$ or $FeCu_2SnS_4$) or tin

[1]*Hofman.*
[2]*Greenwood.*
[3]*Tiede and Birmbraüer.*
[4]*Mohs.*
[5]*Kaye and Laby.*
[6]*Bede and Regnault.*

pyrites, the composition of which is uncertain.

Other Sources:

Hard head dross, waste products, such as tin ash, white metal turnings, scrap slags and tin plate waste.

Mining Localities:

The world's supply comes chiefly from Australia, East India Islands, Bolivia and Cornwall, England. Very large deposits of tin ores are in the Island of Banca, New South Wales, Queensland and Islands of Bilitong. It has been worked in Bohemia, Saxony, Peru, Spain, Germany, Hungary, Malacca in Asia, Chili and at Durango in Mexico. Sparingly in the United States.

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Production of Tin in the United States.[1]

The tin from ores of domestic origin amounted to 140 tons in 1916, and to 150 tons in 1917. Alaska produced during the year of 1917, tin valued at $160.000.

Commercial Metals.[2]

The standard analysis of some of the more important brands:

Billiton—*Sn*, 99.96%; *Sb*, .006%; *Cu*, .023%. Banca—*Sn*, 99.95%; *Sb*, .007%; *Pb*, trace.; *Cu*, .018%; *Fe*, .045%; *S*, trace. Penang—*Sn*, 99.94%; *Sb*, trace.; *As*, .013%; *Pb*, trace.; *Cu*, .016%; *Fe*, .028%; *S*, .04%.

[1]*U. S. Geol. Survey (communication.)*
[2]*The Foundry, Jan.*, 1909.

Singapore—*Sn*, 99.87%; *Sb*, .008%; *As*, .045%; *Pb*, .034%; *Bi*, .003%; *Cu*, .052%; *Fe*, .003%; *S*, .005%. Mt. Bischoff—*Sn*, 99.80%; *Sb*, .015%; *As*, .063%; *Pb*, .037%; *Bi*, .005%; *Cu*, .035%; *Fe*, .042%; *S*, .008%. Chinese No. 1—*Sn*, 99.34%; *Sb*, .031%; *As*, .040%; *Pb*, .434%; *Bi*, .007%; *Cu*, .052%; *Fe*, .10%; *S*, .072%. Chinese No. 2—*Sn*, 98.66%; *Sb*, .039%; *As*, .035%; *Pb*, 1.035%; *Bi*, .012%; *Cu*, .134%; *Fe*, .014%; *S*, .058%. Chinese No. 3—*Sn*, 95.28%; *Sb*, .381%; *As*, .050%; *Pb*, 3.995%; *Bi*, .020%; *Cu*, .106%; *Fe*, .026%; *S*, .116%.

Qualitative Analysis.

Stannous Chloride ($SnCl_2$).

Place .5—1 gram of $SnCl_2$ in a small beaker and dissolve in a mixture of 10 *c. c.* of HCl+10 *c. c.* of water. Add granulated *Zn*, which will precipitate the *Sn* as a spongy mass. Wash the residue with water and dissolve in 20 *c. c.* of hot *HCl*. Divide the solution into 4 parts and treat as follows: (1) Add saturated solution of $HgCl_2$ in excess. A white precipitate of Hg_2Cl_2 indicates the presence of *Sn*.

$$SnCl_2+2\ HgCl_2=SnCl_4+Hg_2Cl_2.$$

If $SnCl_2$ is in excess, the precipitate will be gray due to the presence of metallic *Hg*.

$$2\ SnCl_2+2\ HgCl_2=2\ SnCl_4+2\ Hg.$$

(2) Heat to boiling and add 2 or 3 *c. c.* of $AuCl_3$ solution. A purple-red coloration or precipitate of PURPLE OF CASSIUS is formed.[1] ("probably a mixture of the oxides of tin and gold."—Silliman.) ("its constitution is not established."—Fresenius.)

[1] *"Cassius purple evidently is due to Au formed by the reduction of $AuCl_3$ by Sn, resulting in the hydrogel of stannic acid colored by colloidal Au." (Gruenewald.)*

(3) Add 2 or 3 *c. c.* of $PtCl_4$ solution. A dark crimson coloration indicates the presence of *Sn*. The depth of color depending upon the amount of stannous salt present. The coloration is caused by the reduction of $PtCl_4$ to $PtCl_2$.

(4) Add 1 or 2 *c. c.* of Fe_2Cl_6 solution and same amount of $K_3Fe(CN)_6$ solution. A dark blue solution of Fe_5Cy_{12}, similar to the color of Prussian blue, $Fe_7(CN)_{18}$, denotes the presence of *Sn* (no other reducing reagent present).

H_2S precipitates from neutral and acid solutions, a dark brown precipitate of *SnS*; soluble in *KHO* and *NaHO* solutions, reprecipitated by acids unaltered; soluble in boiling *HCl* with evolution of H_2S; nearly insoluble in colorless $(NH_4)_2S$, but soluble in the yellow sulphide as $(NH_4S)_2SnS$. Reprecipitated by acids as yellow SnS_2, mixed with free *S*; boiling HNO_3 converts it to insoluble metastannic acid[1] ($Sn_5H_{10}O_{15}$?).[2]

KHO, *NaHO*, NH_4HO and alkaline carbonates precipitate from stannous solutions, a white bulky precipitate of SnH_2O_2, soluble in excess of *KHO* and *NaHO*.

Stannous salts, when exposed to the air, absorb oxygen and are rapidly changed to stannic salts, forming insoluble oxychlorides (soluble in water containing free *HCl*) and $SnCl_4$.

$(NH_4)_2S$ produces a precipitate of *SnS* in stannous solutions.[3]

Stannic Chloride. ($SnCl_4$).

[1] *"The product of oxidation of Sn by HNO_3 is not insoluble in acids" Dott. Pharm. J.*, 81, 486.

[2] *Fresenius.*

[3] *Guzman, mentions a new reaction of the Stannous Ions.*-15 *g.* NH_4CNS *are dissolved in* 250 *c.c. of water and* 1 *c.c. of* $(NH_4)_2MoO_4$ *soln. in conc. HCl* (1 *g. in* 10 *c.c.) added. Sn salts give at once a carmine red. The reagent is more senstive than* $HgCl_2$, .1 *mg. of* $SnCl_2$ *in* 1 *c.c. being readily detected. (Chem. Ztg.*, 35, 797.)

Place .5—1 gram of $SnCl_2$ in small beaker and dissolve in a mixture of 10 *c. c.* of water+10 *c. c.* of HCl+3 *c. c.* of HNO_3, boil, and dilute with water. Add excess of HCl and granulated Zn, which will precipitate the Sn. Remove the spongy mass, wash and redissolve in hot HCl, dilute with water and treat as described under stannous chloride 1-2-3-4.

H_2S precipitates from hot acid or neutral solutions, a white flocculent precipitate ("it has not, however, as yet been analyzed." Fresensis.) if stannic solution is in excess. If an excess of H_2S is present, a yellow precipitate of SnS_2 is formed; soluble in KHO, $NaHO$, alkaline sulphides, boiling HCl and aqua regia; soluble in $(NH_4)_2S$ and Na_2S as ammonium and sodium sulphostannates, reprecipitated by acids as SnS_2 unaltered.

Heat on charcoal before the blowpipe in the reducing flame, a small fragment of metallic tin and moisten the white coating of SnO_2 (a slight yellow tinge when hot, and white when cold) with a few drops of $Co(NO_3)_2$ solution and again ignite, a *bluish-green* coloration indicates Sn.

Place a small piece of cassiterite in a small beaker in contact with metallic Zn, cover with HCl and allow to stand a few minutes. A coating of metallic tin is deposited on the surface of the mineral.

Quantitative Analysis.

Iodine Method.

Volumetric Method.—Place .3-.5 gram of the filings in 500 *c. c.* flask, add 40 *c. c.* of HCl and heat gently until the alloy is decomposed. Add now frequently, a little $KClO_3$ to dissolve the slight residue. Add 30 *c. c.* of water and boil 3 minutes. Dilute with water to about 90-100 *c. c.* and add 10 or 12 two-inch iron horse shoe

nails[1] and cork flask with perforated rubber cork, holding a glass tube with a minute outlet. Heat the solution until brisk action begins and allow to simmer on hot sand bath for 30 minutes. Filter luke-warm solution through cotton into 500 *c. c.* flask containing CO_2 (place 2 grams of $HNaCO_3$[2] in flask and acidulate with HCl) and wash flask, filter and nails with oxygen free water (500 *c. c.* water+5 grams $HNaCO_3$+10 *c. c.* of HCl). Add 5 *c. c.* of starch solution and titrate (below 40°C.) with standard I solution to a blue color. Subtract blank and calculate *Sn.*[3]

N/10 *I* Solution.

Place 12.7 grams of pure resubl. *I* and 20 grams of *KI* free from iodate, in small beaker and add 20 *c. c.* of water. Shake frequently until dissolved and dilute to 1000 *c. c.* with water. Mix thoroughly and allow to stand over night before standardizing. Standardize weekly.

$$SnCl_2+I_2+2\ HCl=SnCl_4+2\ HI.$$

$2\ I=Sn.$

$2\ I=126.92\times2=253.84.$

$Sn=118.7\ \times1=118.7$

$118.7:253.84=X:12.692.\qquad X=5.935.$

1000 *c.c.* *N*/10 Iodine *V. S.* containing 12.692 grams $I=5.935$ grams *Sn.*

1 *c.c.* *N*/10 Iodine *V. S.* containing .012692 gram $I=$ .00593 gram *Sn* (theoretical).

Standardize the *I* solution by either of the two following methods:

[1]*Hallett uses a Ni sheet* 1.5 *x* 4 *in. (Eng. Min. J.,* 97, 1151–3.*)*

[2]*Or marble cubes.*

[3]*To prevent the oxidation of the* $SnCl_2$ *solution, Smoot has devised a small apparatus. (Eng. Mining J.* 106, 25–6(1918); *Chem. Abst. Vol.* 12 *No.* 17, *pp.* 1740.*)*

(a) Place .2–.3 gram of pure *Sn* in 500 *c. c.* flask and treat as described under the determination of tin.

$$1\ c.c.\ I\ \text{solution}^1 = \frac{.2065\ \text{gram}\ Sn}{37.45 - .1\ c.c.} = .005529\ \text{gram}\ Sn.$$

No. 2 Babbitt.

$$\frac{.005529 \times 6.55 - .1\ c.c.}{.3\ \text{gram}} \times 100 = 11.88\%\ Sn.$$

Mixture calculation=12.00% *Sn* and, as the commercial metal contained 99.70%, the actual content was 11.96% *Sn*.

(b) Place .2 gram of pure As_2O_3 in 250 *c. c.* beaker, add 15 *c. c.* of a 10% solution of *NaHO*, and shake until dissolved. Add 20 *c. c.* of water, a small piece of litmus paper and render solution slightly acid with dilute *HCl*. Cool, add 50 *c. c.* of a saturated filtered solution of $HNaCO_3$ and 5 *c. c.* of starch solution. Titrate immediately with standard *I* solution to a blue color.

$$As_2O_3 + 4\ I + 4\ HNaCO_3 = As_2O_5 + 4\ NaI + 4\ CO_2 + 2\ H_2O.$$

$$As_2O_3 + 2\ H_2O + 4\ I = As_2O_5 + 4\ HI.$$

$2\ I = Sn.$
$2\ Sn = As_2O_3 = 4\ I.$
$2\ Sn = 118.7 \times 2 = 237.4.$
$As_2O_3 = 197.92 \times 1 = 197.92.$

$197.92 : 237.4 = .2\ \text{gram}\ As_2O_3 : X.$ $\quad X = .2399\ \text{gram}\ Sn.$

[1] *Old solution.*

$$1\ c.\ c.\ I \text{ solution}^1 = \frac{.2399 \text{ gram } Sn.}{43.4 - .1\ c.\ c.} = .005540 \text{ gram } Sn.$$

No. 2 Babbitt.

$$\frac{.005540 \times 6.55 - .1 \text{ c. c.}}{.3 \text{ gram.}} \times 100 = 11.91\%\ Sn.$$

Determination of *Sn* in Commercial Metal.
Iodine Method.

Volumetric Method.—Place .2-.3 gram of the very fine filings or borings in 500 *c. c.* flask, previously filled with CO_2. Add 40 *c. c.* of *HCl* and cork flask with rubber stopper holding a Kroonig valve. Place on hot plate and heat gently to about 80°-90°C. until the metal is dissolved. Remove stopper, add 50 *c. c.* of water and 6 two-inch horse shoe nails that have been bent in the form of loops and fastened to a piece of fine platinum wire, the end of which projects outside of the flask. Place the stopper in the flask and heat until brisk action begins; then allow to simmer on hot plate or sand bath for 30 minutes. Cool the flask and contents quickly with ice water, remove the nails and wash thoroughly with oxygen free water. Add 5 *c. c.* of starch solution and titrate to a blue color with standard *I* solution. Subtract blank and calculate *Sn*.

(a) 99.73% *Sn*. (b) 99.68% *Sn*.

.2 gram As_2O_3=.2399 gram *Sn*.

$$(1)\ 1\ c.c.\ N/10\ I \text{ sol.}^2 = \frac{.2399 \text{ gram } Sn.}{40.30 - .1\ c.\ c.} = .005967 \text{ grm. } Sn.$$

[1]*Old solution.*
[2]*New Solution.*

$$(2)\ 1\ c.c.\ N/10\ I\ \text{sol.}^2 = \frac{.2399\ \text{gram}\ Sn.}{40.35 - .1\ c.c.} = .005960\ \text{grm.}\ Sn.$$

$$(a)\ \frac{.005963^3 \times 33.95 - .25\ c.c.\ (\text{blank})}{.2015\ \text{gram.}} \times 100 = 99.73\%\ Sn.$$

$$(b)\ \frac{.005963^3 \times 34.00 - .25\ c.c.\ (\text{blank})}{.2019\ \text{gram.}} \times 100 = 99.68\%\ Sn.$$

Detection of HIO_3 in KI.

Dissolve 1 gram of KI in 20 *c. c.* of water, freshly boiled and cooled. Add 5 *c. c.* cold starch solution and 3 drops of dilute H_2SO_4 (1 : 3). No blue coloration in 1 minute indicates less than .0001% of I_2O_5. (Merck). Starch Solution.

Mix .5 gram of corn starch with 250 *c. c.* of cold water and heat to boiling. Cool, decant the clear solution and preserve for use.

(A) **Electrolytic Method.**—Place .5-1 gram of the finely divided alloy in 150 *c. c.* beaker, cover with 20 *c. c.* of water, add 2.5 grams of $H_2C_4H_4O_6$ and heat to dissolve. Add 10 *c. c.* of HNO_3(1.42), and heat gently until the alloy is decomposed. Dilute to 50 *c. c.* with water, add a concentrated solution of $NaHO$ until the first precipitate redissolves and the solution is clear. Add 20 *c. c.* of colorless saturated solution of Na_2S (1.20) and allow to stand on hot plate about thirty minutes. Filter into 400 *c. c.* beaker and wash thor-

[2] *New solution.*

[3] *Average.*

oughly with hot dilute Na_2S solution (2%), keeping the volume of the solution down as much as possible. Add to filtrate, dilute H_2SO_4(1 : 1) until the solution is slightly acid, stir thoroughly, allow to settle if possible and decant on 12½ *c. m.* qualitative filter (use two separate filters if necessary). Transfer precipitate to original beaker with a fine jet of water, return funnel and filter to rack and dissolve the remaining sulphide on filter with 25 *c. c.* of $(NH_4)_2S$ solution, diluted to 50 *c. c.* with hot water. Wash the filter thoroughly with hot water and evaporate solution to about 125 to 150 *c. c.* Dissolve the residue in beaker with 15 to 20 *c. c.* of $(NH_4)_2S$, heat gently until the solution is clear, then add 5 grams of KCN and heat on steam plate until the solution is nearly colorless. Dilute to 175–200 *c. c.* with water and electrolyze with ND_{100}=1.5–1.6 amperes 3.5–4 volts. Time six hours. Remove cathode as described under the determination of *Sb*, wash with water and then with C_2H_6O. Dry in air bath for thirty minutes at a temperature of 80°–90°C. and weigh as $Sn+Sb$. Subtract the weight or percentage of *Sb* and the difference equals the weight or percentage of *Sn*.

Weight taken=.5 gram.

Used 4 amperes $\left(\frac{1.6}{.40}=4\right)$—7 volts. (four 32 and two 16 *c. p.* carbon lamps in parallel).

(1) Cylinder+deposit=10.4466 grams.
" =10.0391 "

.4075 gram.

$$\frac{.4075 \text{ gram } Sn+Sb.}{.5 \text{ gram alloy.}} \times 100 = 81.50\%.$$

$$81.50\% \ Sn+Sb - 9.20\% \ Sb. = 72.30\% \ Sn.$$

(2) Cylinder+deposit=10.4465 grams.
" =10.0391 "

.4074 gram.

$$\frac{.4074 \text{ gram } Sn+Sb.}{.5 \text{ gram alloy.}} \times 100 = 81.48\%.$$

$$81.48\% \ Sn+Sb - 9.10\% \ Sb. = 72.38\% \ Sn.$$

or,

$$(1) \frac{.4075 \text{ gram } Sn+Sb - .0460 \text{ gram } Sb.}{.5 \text{ gram alloy.}} \times 100 = 72.30\% \ Sn.$$

$$(2) \frac{.4074 \text{ gram } Sn+Sb - .0455 \text{ gram } Sb.}{.5 \text{ gram alloy.}} \times 100 = 72.38\% \ Sn.$$

Weight of cylinder before deposit=10.0391 grams.
Weight of cylinder after cleaning=10.0390 grams.

The presence of KCN will retain the S in solution and will keep it from separating out on the anode, in excess, by forming $KCNS$ with the polysulphides. (Classen).

$$KCN+S=KCNS.$$

At the end of the electrolysis, the solution is colorless and acid, with some free S.

Cleaning Cylinder.[1]

[1]*Nessler jars of* 100 *c. c. capacity, can be used to contain the separate solutions of* HCl, HNO_3 *and* C_2H_4O.

Place the cathode very slowly in hot concentrated HNO_3 and allow it to remain about five minutes. Remove, wash thoroughly with water and place for same length of time in hot concentrated HCl. Wash with water and repeat the acid treatment if necessary. Finally, wash thoroughly with distilled water, ignite gently, cool and weigh and compare weight with that obtained before electrolysis.

(B) **Electrolytic Method.**—Proceed exactly as described in (A) Electrolytic Method, until the alloy is in in solution. Render solution slightly alkaline with a concentrated solution of $NaHO$, still retaining a clear solution without a precipitate; then add 2 grams of $NaHO$ in excess. Add 15 *c. c.* of Na_2S solution (1.15) and treat exactly as in the preceding method until the Na_2S solution of Sn and Sb is obtained. Acidulate solution slightly with HCl and evaporate on hot plate to about 60-75 *c. c.* Add 10 *c. c.* of HCl (1.20) and 2 grams of Na_2O_2 in small portions, stirring meantime, until the solution is clear with the exception of free S. Boil three minutes, filter into 400 *c. c.* beaker and wash filter contents thoroughly with hot water. Place a small piece of litmus paper in solution and render slightly alkaline with NH_4HO. Add 7 grams of acid $NH_4HC_2O_4 .H_2O$ for every .3 gram of Sn present, heat to dissolve if necessary, and when the salt is in solution, add 9 grams of $C_2H_2O_4$. Warm to 60°-65°C, and electrolyze with a current of ND_{100}=1-1.5 ampere. Time 4-4½ hours. Wash the cathode with water without interrupting the current and immerse in C_2H_6O. Dry thirty minutes at 80°-90°C. Cool and weigh.

Weight taken=.5 gram.

(3) Cylinder+deposit=10.4028 grams.
" =10.0407 "

.3621 gram of *Sn*.

$$(3)\ \frac{.3621 \text{ gram } Sn.}{.5 \text{ gram alloy.}} \times 100 = 72.42\%\ Sn.$$

Results from No. 1-2 and 3 are from the same sample of alloy.

Cathode.

A cylinder of platinum wire gauze. 2 inches high and 1 inch in diameter. Diameter of wire .004 inch. 44 mesh. Area 6.3 inches.

Anode.

A platinum foil 1¾ inches×1¼ inches, fastened to a piece of thick platinum wire.

Caution.

When using 4-5 amperes of current, do not allow the anode to come in contact with the platinum gauze of the cylinder, otherwise the gauze will fuse at the point of contact.

Acid $NH_4HC_2O_4.H_2O$. (Ammonium Binoxalate).

Dissolve 124 grams of $(NH_4)_2C_2O_4.H_2O$ in hot water, add 126 grams of $H_2C_2O_4.2H_2O$, stir thoroughly until dissolved and evaporate to dryness. Place in bottle and cork tightly.

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CHAPTER III.

LEAD.

(Plumbum.)

Mentioned in Ex. XV, 10. It was found in the Sinaitic rocks before the time of Moses, and was known to the Israelites and the Hebrews. It was anciently used to purify silver. Observed by Homer. Pliny gave the name of *plumbum nigrum* to lead and *plumbum canidum* to that of tin. The alchemists in their writings, designated the metal by the sign of Saturn.

Properties, etc. Chemical symbol, *Pb*; atomic weight 207.20; tetravalent; *Sp. Gr.* 11.37[1]; molten 10.88 (327°C.)[2]; melting point 326.2°C.[3]. Fuses at 325.°C. Volatilizes at a strong white heat, air excluded. Boils at 1525°C.; specific heat at about melting point .034[4]; latent heat of fusion 4.00 Cal.[5]; heat conductivity (Ag=100) 8.5[6]; increase in volume at about melting point 3.7%[7]; electrical conductivity (Ag=100) 8.3[1]; casting temperature 500°C.[4]; color bluish-gray, generally known as lead gray; strong metallic lustre when freshly cut, but when exposed to the air the surface is soon

[1]*Matthiessen.*
[2]*Pascal and Joumiaux.*
[3]*Person.*
[4]*Hofman.*
[5]*Richards.*
[6]*Scien. Amer.*
[7]*Toeplar.*

oxidized to the oxide or carbonate, which protects it from further corrosion. Structure granular, as shown by certain etched surfaces, also crystals obtained of regular octahedrons. Combinations of cubes and octahedra crystals have been formed in the working of certain metallurgical processes. Crystalline plates of *Pb* are formed by the voltaic action of metallic *Zn* on *Pb* solutions; tough, ductile, very soft and malleable, but tenacity the lowest of any common metal; contracts on solidifying, forming a convex surface; the surface of the molten metal absorbs oxygen rapidly from the air, forming PbO or PbO_2, according to the degree of heat used. The action of distilled or rain water on lead is similar to that of an acid. The $2\ PbCO_3+Pb(HO)_2$ which is formed generally under these conditions, acts as an energetic poison, readily seen in numerous cases of drinking water or beer that has remained over night in lead pipes. The presence of a small amount of $CaCO_3$ or $CaSO_4$ in the water, forms in time a deposit which prevents further action. When water pipes of *Pb* are used, the action of the particular water in question upon the metal is always tested by experiment. The metal becomes hard and brittle by repeated melting, due to the absorption of the oxides; rolled to thin foil but cannot be drawn to fine wire; hardness increased by the presence of *Ag*, *Bi*, *As*, *Zn* and *Sb*. In the analysis of *Pb* by electrolysis, a red deposit which resembles *Cu* is formed on the anode, which gradually disappears as the *Pb* is deposited on the cathode. White lead ($2\ PbCO_3+Pb(HO)_2$) made from $PbSO_4$ or $PbCl_2$ or by the Dutch, Holland, German, English or French methods, is largely used as a pigment, but is generally mixed with $BaSO_4$, $CaSO_4$, $BaCO_3$, chalk or pipe-clay. Basic chloride of lead ($PbCl_2+Pb(HO)_2$)

has been used as a substitute for carbonate of lead. Cassels and Turners yellow, chrome-yellow ($PbCrO_4$), orange mineral (Pb_3O_4), chrome-red ($2\ PbO.CrO_3$), Madder reds, vermillionettes and Brunswick greens are all valuable pigments of *Pb*. Certain mixtures of heavy-spar and white lead are known as Venetian white, 1 part of barium sulphate to 1 part of lead carbonate. Dutch white, 3 parts of sulphate to 1 part of carbonate. Hamburgh white, 2 parts of sulphate to 1 part of carbonate. Average samples of white lead loses 14% of its weight on ignition. Painters *colic*, a chronic disease caused by the skin absorption of *Pb* compounds. The symptoms of the disease generally show in the following order: constipation, loss of appetite, weakness, extreme thirst, stomach pains, lead palsy, epilepsy, and finally total paralysis. Well defined cases of lead poisoning, are shown by the appearance of a blue line at the edge of the gums, showing a deposit of *PbS*. In many cases, the disease can be avoided by cleanliness. Plumbers, who constantly handle metallic lead seem to be exempt from the disease. Lead forms a suboxide, Pb_2O (black), a monoxide, PbO (yellow), a sesquioxide, Pb_2O_3 or $PbO+PbO_2$ (reddish-yellow), a dioxide or peroxide, PbO_2 (brown), and a compound of Pb_2O_3 and PbO_2 of varying composition, but is usually Pb_3O_4 (red). According to Dulong, PbC_2O_4 is decomposed at a heat below 300°C., (oxygen excluded) as follows:

$$2\ PbC_2O_4 = Pb_2O + CO + 3\ CO_2.$$

The monoxide or protoxide, called in commerce litharge, is the resulting oxide produced by heating *Pb* to that degree that it burns with a white light. On a large scale it is manufactured by heating metallic *Pb* until it forms lead ash, a mixture of *Pb* and *PbO*. Upon further heating, it is wholly converted to the

yellow protoxide. It is largely used in the manufacture of glass, fluxing and the glazing of earthenware, as it dissolves SiO_2 with rapidity; the preparation of varnish, boiled linseed and other drying oils; preparing white lead, red lead, miniums, putty, lead plasters, also for the preparation of chlorides, nitrates, acetates and other definite salts of lead. PbO is soluble in $HC_2H_3O_2$, dilute HCl and HNO_3, soluble in KHO, $NaHO$ and solutions of sugar, almost insoluble in water (1:12,000). Some of the salts of Pb have a sweetish taste, noticed in the acetate or sugar of lead. Certain hair dyes contain acetate of lead and an excess of free sulphur. Litharge is very much used in pharmacy and is never used internally. Mixed with olive oil it forms lead plasters, used for abating inflammation, and for other purposes.

Lead Di-Per-Superoxide, or dark-brown PbO_2 is formed when Pb_3O_4 is treated with cold dilute HNO_3.

$$Pb_3O_4+4\ HNO_3=PbO_2+2\ Pb(NO_3)_2+2\ H_2O.$$

This mixture of PbO_2 and $Pb(NO_3)_2$, is termed red-lead or oxidized minium by match manufacturers. Combined with phosphorus it is largely used as a mixture for lucifer matches. Miniums are intermediate oxides of Pb of variable composition, according to the temperature and care in manufacture. Red lead or Pb_3O_4, is a mixture of PbO and PbO_2 and is formed by roasting PbO or $PbCO_3$ with frequent stirring, for a certain time and at a constant temperature of about 700°F.

$$PbCO_3=PbO+CO_2.$$
$$3\ PbO+O=Pb_3O_4.$$

It is the base of many red pigments and is used for the manufacture of flint glass, cements and many other purposes similar to that of PbO. Lead alloys readily with Sb, Bi and Sn, but said to absorb not more than

1.5% *Zn*, .07% *Fe* and about the same amount of *Cu*. Used largely in the manufacture of the following valuable alloys: White metal, .0-81%; antifriction alloys, .0-88%; plumbers' and tinners' solder, 50%; type-metal, 4.-90%; organ pipes, usually 96%; Chinese tea-chest lead, 87%; ship's nails, 33%; expanding alloy, 75%; soft solder for pillow blocks, 85%; Hoyle's alloy, 42%; Wood's metal, 25%; Rose's alloy, 50%; Onion's alloy, 30%; Newton's alloy, 31%; Tinol (solder), 80%; Magnolia metal, 80%; Lipowitz's metal, 26%; Ajax plastic bronze, 30%; shot metal, 97%; Darcet's metal, 25%; Camelia metal, 15%; Chinese bronze, 15%; Lichtenberg's metal, 30%; Makenzie's alloy, 68%; Phosphorus bronze, 10%; Guthrie's metal, 19%. Lead pipes that are placed in the earth should be coated with asphaltum to prevent corrosion. In one case, lead pipe that had been in the earth twenty-four years, partly embedded in a cement foundation, showed the transformed mass made of twenty-three concentric alternating rings of yellow PbO and twenty-four of red Pb_3O_4. The PbO being formed during the winter and Pb_3O_4 during the summer. Lead covered cables on wooden supports have been corroded due to the moisture on the supports absorbing organic acids from the wood. The acid produced by white ants has been known to destroy the lead covering of cables. Robinson reports two cases of lead poisoning, caused by using as a face powder a cosmetic labeled flake white, a subcarbonate of lead. Rubber cloth containing lead in the rubber compound, has caused poisoning. The amounts found were .02% and .12% PbO_2. The gases from burning stearin candles containing lead stearate has caused illness and headaches. The dryness under which tea is packed in lead foil prevents any danger of lead poisoning. It has

been said that *sick* lead contains more or less chloride. Lead-lined piping is used in the U. S. navy for all salt water pressure piping over 1½ in. to 5½ in. in diameter, and precautions are necessary to prevent lead poisoning. The *Pb* dissolving capacity of water decreases gradually as the inside of the water pipes become lined with a mineral deposit, until practically the water is almost free from *Pb*. Water from peat-covered moorlands will take up 1 to 2.5 grains of *Pb* per gallon. The addition of 1.5 grains of $CaCO_3$ before filtration and 1.5 grains of CaO (clear solution of $Ca(HO)_2$), after filtration will prevent the solution of lead. Alkaline as well as acid solutions, sea-water, cement water and especially lime water attack metallic *Pb*. A Berkefeld filter retains practically all of the lead present in potable water, that has been taken up from *Pb* pipes. Lead poisoning has been caused by eating food prepared in much used common pottery, due to fatty material penetrating the glaze, and upon reheating, the fat containing *Pb* compounds again returns to the surface. Many cases of lead poisoning among lead-workers, are caused by particles of *Pb* taken in the food and drink, showing cleanliness is essential. The discoloration of canned foods in the majority of cases, is caused by the metallic sulphides that are formed by the action of H_2S, which either forms by the reaction of sulphides with vegetable acids or bacterial action due to insufficient sterilization. Lead caps used on food containers containing vinegar, is considered dangerous, as mustard has been found badly contaminated with *Pb*. Acute lead poisoning in man from *Pb* content of earthenware glaze, requires a solution of not less than 20 grams of lead compounds per liter, but repeated doses of a few *mg.* causes chronic poisoning. Snuff wrapped in *Pb* foil containing 89%

Pb caused fatal lead poisoning. The snuff contained 1.75–1.90% *Pb*. Lead arsenate ($Pb_3(AsO_4)_2$) is used extensively as a spray to control the ravages of many leaf eating insects. Lead is largely used in building, leaden chambers for the manufacture of H_2SO_4, tanks and pans for chemical manufactories, water and gas pipes, batteries, shot, rifle balls, alloys and for many other purposes. Lead has the property of flowing in the viscous state and of being welded by pressure in the cold. *Pb* and *Sn* when melted together, unite in all proportions. *Pb* alloys readily with *As*, but with *Zn* and *Fe* only in limited amounts. *Pb* and *Bi* unite in various proportions. *Pb* and *Cu* alloys form more readily when *Cu* is in excess. Calvert and Johnson found expansion in all *Sb-Pb* alloys. *Pb* and *Hg* form amalgams containing as high as 33% *Pb* which remain in the liquid state. Hardness of *Pb* (*talc*=1) 1.5[1]; specific heat between *O*° and 100°C., .0314; at 15°–100°C., .0309; at 300°C., .0338; molten, .0402; for *t*°C., *Sm* (*o* to *t*), $.02925+.000019t^2$; coefficient of linear expansion per degree C. (*O*°–100°) .0000295[3]; tensile strength at ordinary temperature (pounds per square inch) cast, 2,050; coefficient of rigidity,[4] $.562\times10^{11}$; Bulk Modulus,[4] 5.00×10^{11}; Young's Modulus,[4] 1.62×10^{11}. Specific gravity of commercial lead (98.30% *Pb*) 11.33. Weight of 1 cubic foot, 707.27 pounds. Shrinkage of castings per foot, 5/16 or .3125 of an inch. *HCl* and H_2SO_4 have but little action upon the metal, but is readily soluble in hot dilute HNO_3.

Metallurgical Processes:

The oldest type of furnace was used in England during the Roman possession. They were termed ***boles*** by the

[1]*Mohs.*
[2]*Bede and Regnault.*
[3]*Hofman.*
[4]*Kaye and Laby.*

leadworkers of that time and were of the most simple construction. Charcoal was used as a fuel and the ore melted with a natural blast. After the charge was reduced the melted metal was tapped from the bottom of the furnace. The next form of furnace was the ore hearth, with bellows blast worked by water power. This form of furnace is still in use in some localities. Later, certain distinct processes were used, viz.: (a)air reduction process; (b) carbon reduction process; (c) precipitation process. These methods of reduction or modifications of the same are now known as, (1) Carinthian process; (2) Tarnowitz process; (3) English process; (4) French or Brittany process; (5) Blast reduction process; (6) Hearth process; (7) Precipitation process. The type of furnaces used are: Reverberatory, shallow-hearths, converters, low and high shaft blast furnaces.

Blast furnaces are now used in the United States, Australia, Greece and Mexico. The capacity of some of the furnaces are from 140 to 275 tons of lead per 24 hours.

Natural Sources:

Native lead (Pb), seldom found in the free state. Sometimes alloyed with a little Ag or Sb. GALENITE, (PbS); CERUSSITE, ($PbCO_3$); anglesite, ($PbSO_4$); minium (Pb_3O_4); pyromorphite, ($Pb_5Cl(PO_4)_3$ or $3\,Pb_3P_2O_8 + PbCl_2$); vanadinite, ($Pb_5Cl(VO_4)_3$); wulfenite, ($PbMoO_4$); bouronite, ($PbCuSbS_3$); clausthalite, ($PbSe$); crocoite, ($PbCrO_4$); jamesonite, ($Pb_2Sb_2S_5$); mimetite, ($Pb_5Cl(AsO_4)_3$); descloizite, (($PbZn$)($PbOH$) VO_4); zinckenite, ($PbSb_2S_4$); matlockite, (Pb_2Cl_2O); mendipite, ($Pb_3Cl_2O_2$); lanarkite, ($PbO+PbSO_4$); leadhillite, ($PbSO_4+3\ PbCO_3$); phosgenite, ($PbCl_2+PbCO_3$); stolzite, ($PbWO_4$); minetesite, ($3\ Pb_3As_2O_8+PbCl_2$); zorgite, (($PbCu$)Se); lehrbachite, ($PbHgSe$);

castillite, ($PbCuFeAgZnS$); naumanite, ($PbAgSe$); chiviatite, ($2(PbCu)S+3\,BiS_3$); sartorite, ($PbS+AsS_3$); jordanite, ($PbAsS$); plagionite, ($PbS\,Sb$); brongniardite, ($2(PbAg)S+SbS_3$); cosalite, ($2\,PbS+BiS_3$); dufrenoysite, ($2\,PbS+AsS_3$); freieslebenite, ($5\,(PbAg)S+2\,SbS_3$); boulangerite, ($3\,PbS+SbS_3$); epiboulangerite, ($S\,PbSb$); schirmerite, ($PbAgBiS$); kobellite, ($3\,PbS+(BiSb)S_3$); aikinite, ($3\,(PbCu)S+BiS_3$); polytelite, ($S\,PbSbAgFe$); meneghinite, ($4\,PbS\,SbS_3$); geocronite, ($5\,PbS+(SbAs)S_3$); plattnerite, (PbO_2); phoenicochroite, ($3\,PbOCr_2O_3$); jossanite, ($PbOZnOCrO_3$); polysphaerite, ($((PbCa)_3(PO_4)_2+(PbCa)_2PO_4Cl)$); kampylite, ($Pb_3((AsP)O_4)_2+Pb_2(AsP)O_4Cl$).

Other Sources:

Dross, from lead refining; lead matte, from smelting lead ores containing PbS with FeS and CuS as impurities; lead slags, from smelting lead processes; hearth and furnace material, saturated with PbO.

Mining Localities:

United States, England, France, Sweden, Spain, Scotland, Germany, Greece, Belgium, Italy, Austria-Hungary, Norway, Russia, Asiatic Turkey, Mexico, Canada, Japan, China and Australia.

References:

Lead-Smelting. Iles. (*d*).
Lead-Smelting and Refining. Ingalls. (*e*).
Lead Refining by Electrolysis. Betts. (*d*).
Metallurgy of Lead and the Desilverization of Base Bullion. Hofman. (*e*).
Metallurgy of Lead and Silver. Part I., Lead. Collins. (*e*)
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Lead and Zinc in the United States. Ingalls. (*e*).
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Notes on Lead Ores. Fairie. (*e*).
Notes on Lead and Copper Smelting. Hixon. (*b*).
A Precis of Lead Smelting. Longridge. (*e*).
Metallurgy of Lead, including Desilverization and Cupellation. Percy. (*e*).
Notes for a History of Lead. Pulsifer. (*e*).
Lead Smelting. Collis. (*u*).
Lead Poisoning and Lead Absorption. Legge-Goadly. (*k*).

Primary Lead Smelted or Refined in the United States.[1]
Domestic Ores.

During 1914, 534,482 tons; 1915, 555,055 tons; 1916, 571,134 tons. The lead content of ore mined in the United States in 1917, was about 640,000 tons.

Commercial Metals.

The following analyses indicate the purity of the metal:

Refined lead[2]—*Pb*, 99.984%; *Sb*, .0057%; *Cu*, .0014%; *Fe*, .0023%; *Zn*, .0008%; *Ni*, .0007%; *Bi*, .0055%. Refined lead[3]—*Pb*, 99.28%; *As*, .16%; *Sb*, *tr.*; *Fe*, .05%; *Cu*, .25%; *Ag*, .53%. Raw lead[3]—*Pb*, 97.72%; *As*, 1.36%; *Sb*, .72%; *Fe*, .07%; *Cu*, .25%; *Ag*, .49%. Hard lead[3]—*Pb*, 87.60%; *As*, 7.90%; *Sb*, 2.80%; *Fe*, *tr.*; *Cu*, .40%. PARKES' process lead (American)—*Bi*, .066%—.110%; *Sb*, .0028%—.0076%; *As*, .00025%—.009%. Electrolytic lead—*Ag*, .29 oz. per ton; *Cu*, .0010%; *Sb*, .0066%; *Bi*, .0024%; *As*, *tr.*; *Fe*, .0028%.

Qualitative Analysis:

Dissolve 1 gram of the metal in 20 *c. c.* of dilute HNO_3(1:2) and dilute to 50 *c. c.* with water. Boil for

[1] *Press Bulletin, Jan.,* 1918. *U. S. Geol. Survey. (Siebenthal.)*
[2] *Hampe.*
[3] *Reich.*

a few minutes and filter if necessary, on double filter. Divide filtrate in 3 parts.

(1) Add a few drops of strong HCl: white precipitate of $PbCl_2$ is formed, soluble in hot water; converted by NH_4HO to white lead oxychloride[1] ($PbCl_2$. 3 PbO) almost insoluble in water.

(2) Add dilute H_2SO_4(1:1): white precipitate of $PbSO_4$; soluble in hot HCl, forming $PbCl_2$; slightly soluble in hot concentrated HNO_3; soluble in boiling concentrated H_2SO_4, reprecipitated by the addition of water; soluble in aqua regia, $NaHO$, KHO and hot NH_4HO solution; quite soluble in hot solutions of $NH_4C_2H_3O_2$ and $NaC_2H_3O_2$, reprecipitated by $KCrO_4$ as $PbCrO_4$; insoluble in $HC_2H_3O_2$; soluble in solutions of $NaHO$, KHO and dilute HCl.

(3) Add slowly a solution of KI: dark yellow precipitate PbI_2; soluble in excess of KI and dilute HCl.

Heat a small fragment of Pb on charcoal with the reducing flame: coating of brownish-red when hot, light yellow when cold.

H_2S and $(NH_4)_2S$ precipitate from moderately acid and neutral solutions of Pb, a black precipitate of PbS; insoluble in $(NH_4)_2S$; decomposed by hot dilute HNO_3 (1:3) and the solution contains all the Pb as $Pb(NO_3)_2$. Medium concentrated HNO_3 converts the sulphide to the soluble nitrate and insoluble sulphate, with unoxidized sulphur. Fuming HNO_3 converts PbS to insoluble $PbSO_4$ and also oxidizes the sulphur. If HCl is present in excess, a red precipitate of lead chloro-sulphide[1] may form, which is converted to PbS with excess of H_2S.

Na_2CO_3: white precipitate of 2 $PbCO_3.Pb(HO)_2$[1]; slightly soluble in excess, especially if the solution is heated.

[1]*Fresenius.*

$NaHO$, KHO and NH_4HO form white precipitates of hydrates mixed with basic salts; soluble in $NaHO$ and KHO solution, insoluble in NH_4HO.

Quantitative Analysis.

Alexander's Method Modified.

Volumetric Method.—Place 1 gram of the finely divided alloy in 250 *c. c.* beaker, add 20 *c. c.* of HNO_3(1.42) and boil gently until the fumes have disappeared. Evaporate to dryness. Cool, moisten with 5 *c. c.* of HNO_3(1.42), add 50 *c. c.* of water and boil vigorously five minutes. Stir thoroughly, filter into 250 *c. c.* marked flask and wash beaker, filter and contents thoroughly with hot water containing a few drops of HNO_3. Place filter containing the residue in original beaker, add 50 *c. c.* of $(NH_4)_2S$, heat nearly to boiling and allow to stand on hot plate, below the boiling point for fifteen minutes. Filter and wash with hot water containing 2% $(NH_4)_2S$. Place filter and contents in beaker, cover with 40 *c. c.* of dilute HNO_3(1:3) and boil gently until the black sulphides are dissolved. Filter, wash with hot water and evaporate the filtrate and washings if necessary, and add to solution in 250 *c. c.* flask. Cool, dilute to the mark and mix thoroughly. Take 50 *c. c.* of solution with pipette ($1 \div 250 \times 50 =$ .2 gram) and place in 250 *c. c.* beaker. Add 10 *c. c.* of NH_4HO(1:1) and a small piece of litmus paper. Acidulate solution with $HC_2H_3O_2$ (about 2 *c. c.* of 50% solution) and dilute to 100 *c. c.* Heat to boiling and titrate with standard $(NH_4)_6\ Mo_7O_{24}.\ 4\ H_2O$ solution, using a dilute solution of tannic acid as an indicator. (.1 gram of tannic acid dissolved in 20 *c. c.* of water). Standard $(NH_4)_6Mo_7O_{24}.\ 4\ H_2O$ Solution.

Dissolve 8.53 grams of the salt in water and dilute to 1000 *c. c.* Standardize solution with a babbitt of known *Pb* content, which has been precipitated as $PbSO_4$ and weighed in a Gooch crucible. 1 *c. c.* of solution= .01 gram of *Pb*. (theoretical.)

$$(NH_4)_6Mo_7O_{24}.\ 4\ H_2O+7\ Pb(C_2H_3O_2)_2=$$
$$7\ PbMoO_4+6\ NH_4C_2H_3O_2+8\ HC_2H_3O_2$$

$7\ Pb=(NH_4)_6Mo_7O_{24}.\ 4\ H_2O$

$Pb=207.2\times7 \qquad =1450.4$

$(NH_4)_6Mo_7O_{24}.\ 4\ H_2O=1236.316\times1=1236.316$

$1236.316:1450.4=8.53:X \qquad X=10.00$ grams *Pb*.

1000 *c. c.* of Ammonium Molybdate *V. S.* containing 8.53 grams of $(NH_4)_6Mo_7O_{24}.\ 4\,H_2O$=10.00 grams *Pb*.

1 *c. c.* of Ammonium Molybdate *V. S.* containing .00853 gram of $(NH_4)_6Mo_7O_{24}.\ 4\ H_2O$=.01 gram *Pb*. (theoretical.)

Accuracy of Method.

No. 1=69.37% *Pb*.	No. 4=69.37% *Pb*.
" 2=69.37 " "	" 5=69.37 " "
" 3=69.37 " "	" 6=69.37 " "

No. 2 Babbitt.

$$\frac{.00991\times14\ c.\ c.}{.2\ \text{gram.}}\times100=69.37\%\ Pb.$$

Mixture calculation=69.50% *Pb*.

It is much better to standardize the molybdate solution with an alloy of known *Pb* content than to use metallic lead marked *C. P.* containing an uncertain percentage of *Pb*. The above also applies to $PbSO_4$ as means of standardization, as the $PbSO_4$ may absorb moisture and not be in the same condition as when freshly ignited.

The modification of the Alexander method is as follows: Avoiding the precipitation of *Pb* as $PbSO_4$ and the separation of traces of *Pb* from *Sn*, *Sb* and *As* in HNO_3 residues.

It would be of interest for the student to make the following experiment:

Place about .25 of a gram of moist $PbSO_4$ in 150 *c. c.* beaker. Add 50 *c. c.* of $(NH_4)_2S$, stir thoroughly, heat nearly to boiling and allow to stand on hot plate below the boiling point for fifteen minutes. Filter, wash with dilute $(NH_4)_2S$ and transfer precipitate from the filter to original beaker with a little water. Add 40 *c. c.* of dilute HNO_3 (1 : 3) and boil gently until the sulphide is dissolved. Filter on small filter and wash with hot water. Place filter in porcelain crucible, moisten with HNO_3, dry and ignite carefully. Cool the crucible, moisten the ash with a few drops of *HCl* and 1 or 2 drops of HNO_3 and evaporate to dryness. Moisten the slight residue with a few drops of *HCl*, add 2 or 3 *c. c.* of water, heat to boiling and filter on a very small filter. Wash filter with a little hot water, add 4 or 5 drops of H_2SO_4 to filtrate and evaporate to SO_3 fumes. Cool, add 10 *c. c.* of water and allow to settle.

The absence of even traces of $PbSO_4$, clearly indicates that the $PbSO_4$ was converted entirely to *PbS* by the action of $(NH_4)_2S$.

Gravimetric Method.—Place .5 gram of the finely divided alloy in 400 *c. c.* beaker, add 2 grams of $C_4H_6O_6$ and 5 *c. c.* of HNO_3 (1.42). Heat gently until the alloy is decomposed and add *HCl*, a few drops at a time until the metal is dissolved. Add 35 *c. c.* of water to dissolve the soluble salts, leaving a clear solution with no residue. Place a small piece of red litmus paper in the solution

and add a strong solution of $NaHO$ until the solution is strongly alkaline (the precipitate first formed will redissolve as the solution becomes more alkaline and will have a blue color, if more than traces of Cu or Ni are present). Dilute with water to 150 *c. c.* and add 15 *c. c.* of a colorless solution of Na_2S (1.20), stir thoroughly and allow to stand on plate about thirty minutes. Filter and wash with a dilute solution of Na_2S (1 *c. c.* of Na_2S solution diluted to 100 *c. c.* with water) and the last time with hot water. Transfer the precipitate from the filter to the original beaker with a little water, add 15 *c. c.* of fuming HNO_3 and boil down as low as possible. Meantime, place the filter in a small beaker, cover with 25 *c. c.* of hot dilute HNO_3 (1:3) and heat to dissolve the adhering sulphides. Filter, wash with hot water and add filtrate to main solution, to which add 5 *c. c.* of H_2SO_4 (1.84) and evaporate to SO_3 fumes. Cool, add 75 *c. c.* of water, heat to dissolve the soluble sulphates, allow to settle and filter on a weighed porcelain Gooch crucible. Wash five times with hot water containing 1% H_2SO_4 and finally with 40-50 *c. c.* of C_2H_6O and reserve filtrate and wash water for the determination of Cu, Fe and Zn. Dry crucible and contents on hot plate, place crucible on platinum crucible cover and ignite for five minutes. Cool and weigh as $PbSO_4$, which contains .6832 per cent of Pb.

No. 2 Babbitt.

Weight of Gooch crucible+$PbSO_4$=21.0002 grams.
" " " " =20.4925 "
" " " .5077 gram.

$$\frac{.5077 \times .6832}{.5 \text{ gram.}} \times 100 = 69.37\% \ Pb.$$

If a Gooch crucible is not available, proceed exactly as above until the precipitate of $PbSO_4$ is ready to filter. Filter on small ashless filter, wash four or five times with hot water containing 1% H_2SO_4 and finally with 40-50 *c. c.* of C_2H_6O. Dry filter and contents, transfer the precipitate as much as possible to a clean watch glass and place the filter in weighed porcelain crucible and moisten thoroughly with HNO_3. Dry, ignite carefully at a low temperature, cool, add 2 *c. c.* of HNO_3, 1 drop of HCl and 1 or 2 drops of H_2SO_4 and evaporate to dryness. Repeat the addition of acids as above, evaporate and ignite carefully. Cool, add the precipitate, ignite, cool and weigh as $PbSO_4$.

The above precautions must be carefully observed in igniting the filter and reconverting all Pb (reduced by the carbon of the filter) to $PbSO_4$, otherwise there will be a loss due to oxidation and volatilization and by weighing small particles of Pb as $PbSO_4$.

Excellent comparative results can be obtained by filtering the $PbSO_4$ on a weighed filter (dried for one hour in air bath at 100°C.) washing with hot water containing 1% H_2SO_4 and then thoroughly with 95% C_2H_6O, drying the filter and contents in air bath for one hour and weighing as $PbSO_4$.

A sample of solder gave by this method, (a) 54.42% *Pb*. (b) 54.42% *Pb*.

Determination of *Pb* in Commercial Metal.

Gravimetric Method.—Place .5 gram of the finely divided metal in 250 *c. c.* beaker and add 10 *c. c.* of HNO_3 (1.42)+20 *c. c.* of water. Warm gently until the metal is dissolved, add 3 *c. c.* of HCl and boil for a few minutes. Cool, add 10 *c. c.* of H_2SO_4 (1.84) and evaporate to SO_3 fumes. Cool, add 50 *c. c.* of water, heat to boiling and allow to settle. Filter on weighed

porcelain Gooch crucible, wash five times with hot water containing 1% H_2SO_4 and finally with 35–40 *c. c.* of 95% C_2H_6O and continue the determination as usual. Accuracy of Method.

(a) 98.325% *Pb.* (b) 98.284% *Pb.*

According to the analytical experiments of Fresenius, 1 part of $PbSO_4$ is soluble in 22816 parts of pure water and 1 part of this salt is soluble in 36504 parts of water containing free H_2SO_4, also, that there is no decrease in weight on the continued ignition of $PbSO_4$.

A modified Gooch crucible holder is sold under the name of "Esco" by Eberbach and Son, Ann Harbor, Mich. This is really a good apparatus and excludes entirely the use of rubber tubing.

The asbestos for the Gooch crucible should be treated for a few hours in each of the following acids, HCl, HNO_3 and H_2SO_4 (1:5) and allowed to remain in the latter solution until used.

Electrolytic Method.—Proceed exactly as in the gravimetric method until the black precipitate of PbS and CuS is obtained. Wash thoroughly with dilute $(NH_4)_2S$ and finally, once with hot water. Dissolve the sulphides in a mixture of 15 *c. c.* of HNO_3+25 *c. c.* of water, filter and wash with hot water. Dilute filtrate to 150 *c. c.* with water and electrolyze with a current of ND_{100}=1 to 1.5 ampere and 2.5 volts. Time, one to two hours. Temperature 50° to 60°C. When all the metal is deposited, lower the beaker slowly (meantime continue the current), wash the cathode (serving as anode) and deposit with distilled water and immerse in 95% C_2H_6O for a few seconds. Dry in air bath at 160°–190°C., to constant weight. Multiply the weight

of the deposit by a factor that has been found by direct experiment.[1]

Weight taken=.5 gram.

Used 3.7—4 amperes $\left(\frac{1.5}{.40}=3.75\right)$ and 3.5 volts.

(Three 32 and three 16 *c. p.* lamps in parallel).

Time one hour.

Cylinder+deposit=10.2774 grams.
" =10.0400 "

.2374 gram.

.2374	gram	of	PbO_2	after	30	minutes	at	160°C.
.2369	"	"	"	"	60	"	"	"
.2365	"	"	"	"	90	"	"	"
.2363	"	"	"	"	120	"	"	"
.2360	"	"	"	"	150	"	"	"

$$\frac{.2369\times.8411}{.5 \text{ gram.}}\times100=39.85\%\ Pb.$$

$K_2Cr_2O_7$ Method. (Schwarz's method).=40.03% *Pb*.

Factor Calculation.

A sample of alloy containing 14.78% *Pb* was used as a standard. The *Pb* was determined and weighed as $PbSO_4$.

Weight taken=.5 gram.

Cylinder+deposit=10.1281 grams.
" =10.0402 "

.0879 gram.

[1]*Sand found it was best to dip the PbO_2 into alcohol, then into ether and then heat rapidly over a Bunsen. The factor used for the above was .863 to 865. (Sand. Chem. News 100, 269–70.)*

$$\frac{.0879 \times .8662^{1}}{.5 \text{ gram.}} \times 100 = 15.22\% \ Pb.$$

14.78 : 15.22 = X : .8662. X = .8411 = factor.

$$\frac{.0879 \times .8411}{.5 \text{ gram.}} \times 100 = 14.78\% \ Pb.$$

Cylinder and deposit of PbO_2 dried in air bath for one hour at 160°C.

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[1]*Per cent. of Pb in* PbO_2.

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CHAPTER IV.

COPPER.

(Cuprum.)

The first metal employed by man. Known for a long time previous to the Exodus. The metal in the form of bricks and rings was used as a medium of trade by the Egyptians and Babylonians. Obtained by the Greeks and Romans from the Island of Cyprus, whence its name. For this reason the metal was considered especially sacred to Venus and is designated in the writings of the alchemists by the symbol of this goddess. Later it was known as *aes cyprium* and finally by the name of *cuprum*. Ireland used the metal for the means of barter down to the 12th century and it is still in use in the interior of Africa for the same purpose.

Properties, etc. Chemical symbol, *Cu*; atomic weight, 63.57; bivalent; *sp. gr.*, native, 8.94; cast, 8.92; rolled or hammered, 8.95; pure electrolytic, 8.945[1]; at 1083°C., 8.40[2]; melting point, 1083°C.[2]; volatilization commences, 960°C.[3]; visible ebullition, 2310°C.[4]; boiling point, 2100°C.[5]; specific heat at about 15°C., .086[6]; at 20°-

[1]*Hampe.*
[2]*Pascal and Joumiaux.*
[3]*Tiede and Birnbräuer.*
[4]*Greenwood.*
[5]*Fery.*
[6]*Hofman.*

100°C., .0936; at about melting point, .118[1]; molten, .1318; latent heat of fusion, 43.3 Cal. (observed[2]); heat conductivity (Ag=100), 73.6[3]; electrical conductivity, 99.9[4]; casting temperature, 1250°C.[1]; hardness (talc=1), 2.5-3.0[5]; tensile strength at ordinary temperature (pounds per square inch), cast, 24,000; sheet, 30,000; hard drawn, 60,000; soft drawn, 35,500; bolts, 34,000; coefficient of linear expansion per degree C. (0°-100°), .0000179[1]; coefficient of rigidity,[6] 4.55×10^{11}. Bulk Modulus,[6] 13.10×10^{11}. Young's Modulus,[6] 12.3×10^{11}; for t°C., $Sm(O \text{ to } t)$, $.0939+.00001778t^2$; shrinkage of castings per foot, $\frac{3}{16}$ or .1875 of an inch. Structure: Crystals of octahedrons have been found in native copper and in refinery products; cast and electrolytic, granular; rolled and hammered, fibrous. Color, a peculiar yellowish-red, beautiful brilliant luster when polished; has a slightly loathsome taste, and has a disagreeable odor when rubbed; luster destroyed and the metal becomes tarnished by exposure to the air; hard, tough, very malleable and ductile, the latter is greater by increase of temperature; very thin copper leaf has a greenish-blue color due to transmitted light; can be rolled and hammered at a low red heat; the surface of the molten metal exhibits a fine sea green color, and flows readily when free from the suboxide but the flow is sluggish if the oxide is present; not suited for castings as it becomes honeycombed and internally crystalline. This can be avoided by melting the metal under a layer of charcoal, lowering the temperature of the molten metal before casting and using iron molds lined with bone ash. The addition of

[1]*Hofman.*
[2]*Frazier and Richards.*
[3]*Scien. Amer.*
[4]*Matthiessen.*
[5]*Mohs.*
[6]*Kaye and Laby.*
[7]*Frazier and Richards.*

.1% of *Pb* or *Zn* to the molten metal overcomes the expansion and porous structure, but renders the metal cold- and red-short. A small quantity of the suboxide acts in the same manner; behaves like *Ag* on cooling, by expelling previously absorbed gases; when highly heated in contact with air the metal burns with a brilliant green flame and the filings are used in pyrotechny; moist air, H_2S and other corroding gases cause the surface to become covered with carbonate of hydrated suboxide, known as verdigris, which adheres to the metal with great tenacity and protects it from further corrosion; rendered harder by rolling or hammering and softened by heating and quenching in water; the color of the surface of the metal depends upon the temperature of the water in quenching. Cold water produces an orange-red, warm water a rose-red tint. Commercial copper usually contains small quantities of *As*, *Sb*, *Sn*, *Pb*, *Zn*, *Fe* and *S*. The action of certain metals upon copper is said to be as follows: The presence of .05% of *C* renders the metal red-short. (Karsten). Aluminum prevents oxidation of the fluid metal. (Tissier). Zinc, tin and sulphur renders copper red-short. (Erdmann). Iron renders the metal hard and brittle, but the best copper may contain .1 to .15%. (Percy). Antimony in as small amounts as .001% renders the metal unfit for the production of brass plates and wire, while *As* has a similar action. The presence of .001% *Bi* injures the quality of the metal, chiefly by lowering its ductility. (Levol). Copper containing .2 or .3% *Ni* is less adapted for the manufacture of brass than for German silver, and *NiO* renders the metal somewhat brittle. (Genth). Copper containing as high as 1.82% *Si* may be rolled and hammered when cold, but becomes brittle when hot. (Percy). Phosphorus increases the

fusibility and hardness of the metal. Copper containing 1.5% *P* may be rolled, and with a greater percentage, the metal becomes brittle when cold. (Percy). Sodium has a purifying action on copper. (Tissier). The presence of .1 to .3% *Pb* renders the metal no longer suitable for fine brass plates and wire, but it seems to increase its rolling qualities. At a temperature just below its melting point, the metal is very brittle and can be easily broken in a mortar into small fragments; expands in passing from the liquid to the solid state. Brass has been known from a very remote period, and is a very important alloy of *Cu* and *Zn*. By the ancient or calamine method, the alloy was produced by melting metallic copper with zinc oxide and charcoal. It is said that it is only within the last eighty or ninety years, that the direct method has been used by which the alloy was formed by the direct fusion of *Cu* and *Zn*.[1] No doubt the practice began soon after Paracelsus pointed out that zinc was a metal. The term brass has been applied to all the alloys of *Cu* and *Zn*. It generally contains on an average about 30–33% of *Zn*. The ductility and malleability of the alloy increases with the per cent of *Cu*; not so readily oxidized as *Cu* as it is harder and tougher, melts at a lower fusion point and more fluid while molten. The structure is solid and by the addition of from 1 to 2% *Pb* it can be worked on a lathe and the castings finished by filing. The color of the alloy is variable, depending upon the amount *Cu* present. By adjusting the percentage of each metal, the color of the resulting alloy range from red with a faint yellow tint, reddish-yellow, yellowish-red, full yellow, golden-yellow

[1]*The first brass by the direct fusion of Cu and Zn with or without the addition of calamine, was patented and made in* 1781, *by James Emerson of England. (Brannt.)*

and finally to a whitish-yellow as the quantity of zinc is increased. The copper content of Bavarian bronzes is as follows: copper-red, 98.92%; violet, 98.82%; orange, 95.30%; deep-yellow, 81.55%; bright yellow, 82.34%. Muntz's patent metal, an alloy of 60 parts of *Cu* and 40 of *Zn*, is forged into bolts and rolled into sheets while red-hot. The alloy is said to vary from 50% *Zn* and 63% of *Cu*, to 39% *Zn* and 50% *Cu*. Aich-metal, is in reality malleable brass and consists of *Cu* 60%, *Zn* 38.2% and *Fe* 1.8%. If the molten brass is kept in contact with the air for any length of time, the calculated composition is changed due to the combustion and volatilization of the greater part of the *Zn*, which explains the variation in color and analysis from that which the melter intended to obtain in the finished product. Brass should contain only *Cu* and *Zn*, but the alloy usually contains small quantities of *Pb*, *As*, *Sn* and *Fe*. In many cases the presence of these metals are due to the reduction of impure ores of *Cu* and *Zn*, while in others the metals have been intentionally added to change the color, structure, hardness and fusibility. Brass containing about 28.5% *Zn* shows the greatest absolute strength, but the mechanical treatment must also be considered, as the more it is worked or manipulated, the harder and more brittle the alloy becomes. This is remedied by heating the alloy strongly and quenching it quickly in water. The shrinkage of brass castings varies from 5/32 to 3/16 of an inch, depending upon the percentage of *Cu* and *Zn* present and the fusion point is also variable due to the differenc in the melting point of the two constituent metals. The fusing point is rendered lower and the structure more dense, by the slight addition of *Sn*. Copper and zinc when melted together, unite in all proportions and usually

combine with the evolution of heat. Copper alloys readily with *Au*, *Ag*, *Sn*, *Sb*, *Hg*, *Cd*, *Zn*, *Ni*, *Co*, *Al*, *Mn*, *Mg* and slightly with *Mo*, *W*, *Cr*, *Fe*, if the metal is pure. The metal readily absorbs and alloys easily with Cu_2O and Cu_2S. Copper forms the base of many of the following bronzes: ajax plastic, medal and coin, gold, ship-sheathing, machine, trolley-wheel, speculum, turbadium, U. S. Naval, Fontaine-moreau, hydraulic, Morin's, Tobin, phosphor, phosphor-copper, phosphortin, phosphor-lead, phosphor-aluminium, aluminium, silicon-manganese, cupro-manganese, copper-lead, copper-iron, copper-steel (5 to 20% *Cu*), copper-tungsten, copper-cobalt, copper-magnesium, Chinese, Japanese, Peruvian and Turkish. There are also many other alloys of *Cu*, which are fully described in the many excellent works which treat extensively on the subject of alloys.[1] Commercial $CuSO_4.5\ H_2O$ is generally used as a base for copper pigments. The following represent some of the most important colors. Brunswick-green, $CuCO_3 + Cu(HO)_2$. Schweinfurt's-green or emerald-green, also known as Paris-green, is an aceto-arsenite of copper, $(CuOAs_2O_3)_3\ Cu(C_2H_3O_2)_2$. Scheele's-green or mineral-green and blue, is a copper arsenite, $CuHAsO_3$. Wall paper colored with the above arsenites is considered dangerous, due to arsenic poisoning. Such papers are said to give off arsenical vapors or dust, which disseminate through the air and is absorbed by the lungs and skin. Both of these compounds are also used for anti-insect powders. Mitis'-green is an arseniate of copper. Casselman's-green, free from *As*, consists of basic acetates of copper combined with more or less water. This pigment is said to have also the formula of $CuSO_4 + 3\ Cu(HO)_2 + 4\ H_2O$ due to a different

[1] *Brannt, Hiorns, Buchanan, Sexton, Gulliver, Parry, Law.*

method in its manufacture. Lime-blue, a mixture of lime with a weak solution of $Cu(NO_3)_2$ so that the lime is saturated. Oil-blue is essentially CuS. Verdigris is a basic hydrated copper acetate. The blue variety has approximately the composition of $(C_2H_3O_2)_2Cu$, $Cu(HO)_2+5\ H_2O$ and the green variety $2\ Cu(C_2H_3O_2)_2+Cu(HO)_2$. The salt contains a variable proportion of bibasic and tribasic copper acetates. Verdigris forms the base of green-inks, green-oils, green stains and glazes. The green rust of copper is $CuCO_3$, and should not be confounded with true verdigris. Vienna-green, is a mixture of As_2O_3 and verdigris. Bremen-blue or Bremen-green is essentially hydrated oxide of copper. Brighton-green, $CuSO_4+Pb(C_2H_3O_2)_2+CaCO_3$. Blue-verditer is $Cu(NO_3)_2$ mixed with $CaCO_3$. Bice-blue, native $CuCO_3$. Copper-blue, a mixture of $CuCO_3$ and $CaCO_3$. Egyptian-blue is formed by heating SiO_2, CaO, CuO and Na_2O, at a temperature not exceeding 800°F. The resulting product is then ground. There are four oxides of copper, viz., copper tetrantoxide, Cu_4O, olive green powder which rapidly absorbs oxygen when exposed to the air. Copper hemioxide, cuprous oxide or suboxide, Cu_2O, red. Formed by heating metallic Cu and is found native in octahedral crystals, occurs as cuprite or red copper ore. This oxide is used to produce copper glass of a fine ruby color. Cuprous hydroxide, $Cu_3O_3(HO)_2$, bright yellow, absorbs oxygen when exposed to the air and becomes blue. The hydroxide is soluble in NH_4HO forming a colorless solution, which when exposed to the air becomes a dark blue color. Cupric oxide, monoxide or protoxide, CuO, black. Occurs as melacnite or black oxide of copper. Formed by the gentle ignition of hydroxide, carbonate

or nitrate and is quite soluble in acids and is the base of all green or blue salts of copper. Cuprous oxide when ignited in contact with the air changes to CuO. This oxide is used to color glass a fine green. Cupric hydroxide, $Cu(HO)_2$, light blue. Soluble in NH_4HO forming a blue solution. CuO and $Cu(HO)_2$ are both soluble in HNO_3, HCl and H_2SO_4. Copper dioxide, $CuO_2.H_2O$, yellowish-brown powder which decomposes readily into CuO and oxygen. Pure copper is extensively used for submarine telegraphs as it is, with the exception of Ag, the best conductor of electricity. The commercial metal is largely used for a great variety of purposes both technical and domestic. Especially valuable in the manufacture of tubular boilers, vacuum pans for sugar works, brewery, distillery and many kitchen utensils, Ship-sheathing and electrical apparatus. The prehistoric copper miners of Lake Superior used the metal exclusively for hammers, chisels, arrow-points, spear heads, knives, needles, axes and fish-hooks, long before methods for the smelting and the extraction of iron were known. Permanent magnets have been made from nearly pure copper by first heating the metal to redness, plunging in cold water and then magnetizing in a field of over 3000 *c. g. s.* units. The metal retains permanent magnetism amounting to .14 *c. g. s.* Magnetism not due to the presence of iron. Bosh-cooled copper pig is said to contain occluded moisture which is difficult, if not impossible to drive off under about 240°F. A piece of copper alloy taken from a ship's keel, contained originally, 45–55% Cu, 40–45% Zn and about 1% of each of Pb, Mn and Fe. After being exposed to the action of salt water was found to contain 52.7% Cu, 41.1% Cu_2O, 1.44% H_2O, 2.75% Pb, Zn and Fe salts and 2.05% of insoluble material. The Zn had practically

disappeared. The corrosion of *Cu* by salt water, usually produces a scale of Cu_2O. Copper for casting should contain about 99.9%, and the brand also known. The greater the purity, the greater the electrical conductivity. With .03–.80% *As* present, relative conductivity is lowered from 100 to 40. The cold-drawing of copper increases its tensile strength and reduces elongation. A black coating on copper is obtained by moving the objects about in a 5% bath of *NaOH*, to which 1% of powdered $K_2(SO_4)_2$ has been added. Other metals are first *Cu* plated before treatment. The time required for pure *Cu* is about five minutes and for alloys about five to ten minutes. According to Meunier, when electrolytic copper is heated until it is glowing and then plunged into the interior of the burner flame, the metal continues to glow and at the same time colors the flame green, showing that combustion is taking place without flame. It is said that the color of the flame is due to the volatilization of amorphous *Cu* which binds the crystals of the metal together. Repeated melting of copper shows after each melting, a distinctly inferior quality, which is clearly shown by the testing machine. Oxidation and absorption of *S* causes the inferiority. By the introduction of small quantities of *CuO* to molten glasses rich in alkali and either *CaO* or *PbO*, blue colors are obtained. Weintraub has succeeded in casting very pure *Cu* by adding B_6O to the molten metal. Sound castings of high conductivity are obtained from either sand or iron molds.[1] Electrical conductivity as high as 97% has been obtained. Archbutt states that copper fire-box plates containing .66% *As*, .5% *Sb*, .05% *Bi*, .06% *O*

[1] *A small amount of Sr added to molten Cu, is said to produce a harder than ordinary Cu casting free from blow holes. (Iron Age, May 23, 1918.)*

and .63% *As*, .03% *Sb*, .07% *Bi*, .09% *O* withstood hot working and service. The idea then is that the supposition of .0001% *Bi* will change good copper into the worst conceivable is an error. In general, the addition of *Mn*, *Sn* or *P* to *Cu* increases the strength and hardness and lowers the ductility, electrical conductivity and specific gravity. According to Bardwell, the following which is based on the conductivity curves of copper, the zone of cold rolling lies at 0°–150°; the zone of relaxation at 150°–355°; the zone of recuperation at 355°–425°; the zone of complete annealing at 425°–600°, and the bending zone at 600°. Under the microscope, cold rolled *Cu* show slip bands indicating a strained condition. These bands disappear and very small crystals are formed after the metal is annealed in the zone of relaxation. Large crystals are formed in the zone of recuperation and the maximum of regular growth of crystals in the annealing zone. Above this temperature the crystal growth is rapid and with a decrease of ductility and conductivity. Pionchon has shown that when two *Cu* plates are placed in water and the circuit closed with a galvanometer, a deflection is seen when one of the electrodes is tapped. After repeating the test, the reaction becomes less and less and finally ceases entirely. Traces of *Cu* have been identified so minute that no chemical reagent will detect it. To determine the areas of *Cu* coatings of light and heavy deposits, Wilson recommends covering the object entirely with beeswax, removing this from the area in question and the *Cu* determined in the solution as usual. According to Caesar and Gerner, pure *Cu* begins to soften at 200°, most rapidly between 225° and 275°, and is complete between 300° and 350°. The cold-worked condition persists up to 300° and the most rapid softening near 350°. For the dark-gray coloring

of *Cu*, Groschuff recommends dipping the *Cu* casting for ten or fifteen minutes in a boiling solution of 100 *c. c.* of water, containing 12 grams of $CuSO_4.5\,H_2O$ and 1.5 grams of $KMnO_4$. A brown color is produced by dipping the objects in a boiling solution of 12 grams of $CuSO_4.5\,H_2O$ dissolved in 100 *c. c.* of water. Even if scoured brass and glass beakers gave identical results in the determination of extract of malt, tarnished brass beakers influenced the results considerably. According to Ling and McLaren, worts from such beakers contained as high as .1 gram of *Cu* per gallon. Traces of *Cu* have been found in filter paper, including analytical grades. The skin absorption of *Cu* by brass workers has been shown by the detection of the metal in the urine and green sweat stains on the underclothing of the workers. The action of the *Cu* salts, also exert a prophylactic action with respect to caries and oral sepsis. The use of bad gold alloy in the mouth has caused chronic copper intoxication. Hansen states that the fumes of *Cu* from the electric arc furnace are poisonous. The symptoms were great inconvenience in breathing, and twenty-four hours later, severe nausea and soreness similar to that of acute grip. The conditions of ventilation during the melting and pouring were the most favorable, and should it had been otherwise the results would have probably been very serious. According to Graff, the books of a reputable German firm has shown for the greening of preserved vegetables, the following weights of $CuSO_4.5\,H_2O$ that has been used on an average, per kilo of vegetables: 1903, .90 gram; 1904, .71 gram; 1905, .96 gram. From a number of analysis of the products, the $CuSO_4.5\,H_2O$ in the drained vegetables, varies from 200 to 1377 *m. g.* per kilogram, also amounts of copper sulphate smaller than 215 *m. g.* per

kilo do not produce a satisfactory greening of the vegetables. The medicinal dose of sulphate of copper, as a astringent or tonic, is .016 gram gradually increased; as an emetic, .13–.33 gram. According to Liberi-Cusmano-Marsiglia-Zay, copper is constantly found in the fruit of the tomato. The amount varies from .14 *m. g.* to 2.10 *m. g.* per *k. g.* of juice and pulp and from 3.8 *m. g.* to 19.5 *m. g.* per *k. g.* of dry matter. The *Cu* contents of the plants was not due to spraying with *Cu* mixture. Hart states that pressed beef contained small amounts of *Cu* due to the gelatin that was used as a garnish. The *Cu* contents expressed in *m. g.* per *k. g.* were: pressed beef, 0–34; gelatin *A*, 25; gelatin *B*, 104; jelly preparation, 60; and samples of gelatin for family use contained 0–56.3 *m. g.* of *Cu* per *k. g.* Samples of canned spinage has been found to contain from 128 to 275 *m. g.* of *Cu* per *k. g.* The highest permissible limit of *Cu* is placed at 55 *m. g.* per *k. g.* Canned peas of French origin, from the various provinces of Canada, contained in majority of cases an excess of *Cu* exceeding Tunnicliffe's limit of ½ grain per lb. or 71 parts per million. Caraccas, Guayaquil and Bahia cocoas, contain respectively, .020 *g.*, .027 *g.*, .034 *g.* of *Cu* per *k. g.* in the shell-free seeds and .040 *g.*, .014 *g.*, and .035 *g.* respectively in the shells. Sweetened chocolates showed the *Cu* content to be a mean of .012 *g.* per *k. g.* Minute amounts of *Cu* has been found in sample of caffeine. A sample of pomace brandy from Maconnais, showed 15 *m. g.* of *Cu* per liter. The green color of some oysters may not be due to *Cu* but to a green pigment, but as high as 40 *m. g.* of *Cu* has been found in the blue colored variety, while those that were uncolored contained 9 *m. g.* It is said that a small

amount of *Cu* salts in milk has been found to be highly efficient as a preservative.

Metallurgical Processes.

The methods that are used for the extraction of copper from the various ores differ, and the treatment must vary according to the nature of the ore.

(1) Ores containing Oxides.
(2) Pyritical ores.
(3) Low grade ores.
(4) Native copper.

Oxidized ores are usually smelted in shaft-furnaces with coal or coke, and fluxed so as to produce a slag which does not absorb copper. The cupola furnace (German process) is prefered for very rich ores, as it gives a quicker extraction. The resulting product of black copper is then treated in the reverberatory furnace. A special form of cupola furnace is employed for the smelting of oxidized ores rich in iron. If fuel is cheap, rich ores may be smelted in the reverberatory furnace (English process). The ores are often first reduced to black copper before treatment in the above furnace.

Pyritical ores are first roasted or calcined and then treated in a crucible, pit, cupola, shaft, converter, reverberatory or a combined smelting in cupola and reverberatory furnaces with a final product of black copper, which is then further refined to partially remove the impurities. The remainder of the latter, is nearly all removed with the suboxide of copper, by a rapid melting of the metal under a layer of charcoal.

Low grade ores are generally treated by hydrometallurgical methods. The wet copper extraction process is applied to ores which are too poor to admit being

smelted by the dry process. The ores are treated so as to form copper salts which are soluble in water and the copper is precipitated from the solution by metallic iron. In some mines a solution of copper sulphate occurs naturally. The wet methods are also applied to roasted iron pyrites, a by-product of the sulphuric acid works, which generally contains on an average about 3% *Cu*. At the present time the chloridizing and leaching process is applied to low grade oxidized ores containing *Au* and *Ag*. Gravity and flotation methods are much practiced for the concentration of poor copper ores. The following well known methods are used for treating low-grade and complex ores. Sulphidizing and flotation, Mosher-Ludlow process and the Slater process.

Native copper may contain *Au*, *Ag*, *As*, *Sb*, *Pb*, *Zn*, *Fe*, *Ni*, *Co* and when free from the precious metals, the crude copper is treated in the reverberatory furnace with oxidizing fusion and the product further refined by reducing fusion. At the present time refined *Cu* is made almost entirely from the crude metal. It is said that the production of pure copper from the ores and matte has thus far, proved a failure. Electrolytic refining methods are generally used for crude copper containing precious metals. The electric furnace can be used as a substitute for the combustion furnace especially, where the price of fuel is high.

Native Sources.

NATIVE COPPER, (*Cu*) often containing *Au*, *Ag*, sometimes *Bi* or *Hg*. Occurs in threads, wire and in small grains to several tons in weight. In 1854, one mass of native copper (69.28% *Cu*) weighing about 500 tons was found in Minnesota, U. S.[1] In Chili, there is known a copper sand or copper barilli containing 60 to 80%

[1]*Crookes and Röhrig.*

of Cu and 20 to 40% of SiO_2. CHALCOPYRITE, ($CuFeS_2$); CHALCOCITE, (Cu_2S); BORNITE, (Cu_5FeS_4); CUPRITE, (Cu_2O); TETRAHEDRITE, ($Cu_8Sb_2S_7$); MALACHITE, ($Cu_2(OH)_2CO_3$); CHRYSOCOLLA, ($CuSiO_3 . 2 H_2O$); AZURITE, ($Cu_3(OH)_2(CO_3)_2$); ENARGITE, (Cu_3AsS_4); Dioptase, (H_2CuSiO_4); Tenorite, (CuO); Chalcanthite, ($CuSO_4 . 5 H_2O$); Atacamite, ($Cu(OH)Cl . Cu(OH)_2$); Covellite, (CuS); Erubescite, (Cu_3FeS_3). It would be well to mention other copper minerals. Trichalcite, ($Cu_3OAsO_5+5 H$); Thrombolite, (CuO, H, PO_5); Libethenite, (Cu_3OPO_5+CuOH); Olivenite, ($Cu_3(AsO_5, PO_5)+CuOH$); Conichalcite, ($CuOCaO PO_5AsO_5VO_5H$); Bayldonite, ($(PbO, CuO)_4AsO_5+2 H$); Euchroite, ($Cu_3OAsO_5+CuOH+6 H$); Tagilite, ($Cu_3PO_5+CuOH+2 H$); Veszelyite, ($4 CuOPO_5+5 H$); Liroconite, (CuO, AlO_3, AsO_5, PO_5H); Pseudomalachite, ($Cu_3OPO_5+2 CuOH+H$); Erinite, ($Cu_3 OAsO_5+2 CuOH$); Cornwallite, ($Cu_3OAsO_5+2 CuOH +3 H$); Tyrolite, ($Cu_3OAsO_5+2 CuOH+7 H$); Clinoclasite, ($Cu_3OAsO_5+3 CuOH$); Chalcophyllite, ($Cu_3AsO_5+5 CuOH+7 H$); A. Zeunerite, ($CuO, 2 UO_3AsO_5+8 H$); Ammiolite, ($HgCuFeSSbO_5$); Lindackerite, ($2 Cu_3AsO_5+NiO_3SO_3+7 H$); Cuproscheelite, ($CuOWO_3+2 CaOWO_3$); A. Cuprotungstite, ($CuO, 3 WO_3$); Volborthite, ($CuO, VO_5H$); A. Vanadate of Lime and Copper, ($(CuO, CaO)_4VO_3+aq$); A. Hydrocyanite, ($CuOSO_3$); B. Dolerophanite, (Cu_2AsO_3); Domeykite, (Cu_6As); Algodonite, ($Cu_{12}As$); Whitneyite, ($Cu_{18}As$); Eucairite, ($(CuAg)Se$); Crookesite, ($(CuTlAg)Se$); Zorgite, ($(PbCu)Se$); Berzelianite, ($CuSe$); Castillite, ($CuPbFeAgZnS$); Grünauite, ($CuBiNiFeS$); Stromeyerite, ($(CuAg)S$); A. Chalcopyrrhotite, (Cu_4CuS_6); Cubanite, ($CuS+FeS+3$

FeS_2); Barnhardtite, ($2\ CuS+FeS+FeS_2$); Carrollite, ($2(CuCo)S+CoS_2$); A. Spathiopyrite, ($CuCoFeAsS$); Chalcostibite, ($CuS+SbS_2$); Emplectite, ($CuS+BiS_3$); Chiviatite, ($2(CuPb)S+3\ BiS_3$); Binnite, ($3\ CuS+AsS_3$); Bournonite, ($3(CuPb)S+SbS_3$); Stylotypite, ($3(CuFeAg)S+SbS_3$); Wittichenite, ($3\ CuS+BiS_3$); A. Klaprotholite, ($3\ CuS+Bi_2S_3$); Aikinite, ($3(CuPb)S+BiS_3$); Tennantite, ($4(CuFe)S+AsS_3$); A. Julianite, ($SAsCuSb$); Polybasite, ($(9(AgCu)S+Sb)AsS_6$); A. Epigenite, ($CuFeAsS$); B. Famatinite, ($4(3\ Cu_2SSSb_2S_5)+3\ Cu_2SAs_2S_5$); Clayite, ($SAsSbPbCu$); A. Nantokite, ($Cu_2Cl$); A. Tallingite, ($4\ CuH+CuClH$); Percylite, ($PbCuClOH$); Crednerite, ($Cu_3OMn_2O_3$); E. Rabdionite, ($Cu,\ Fe,\ Co,\ Mn,\ O$); Connellite, ($CuOSO_3\ CuCl$); Vauquelinite, ($CuO_3Cr_2O_3+PbO_3Cr_2O_3$); Pisanite, ($(FeO,\ CuO)SO_3+7\ H$); Chalcanthite, ($CuOSO_3+5\ H$); A. Cupromagnesite, ($(CuOMgO)SO_2+7\ H$); Cyanochroite, ($(\frac{1}{2}CuO+\frac{1}{2}KO)SO_3+3\ H$); Brochantite, ($CuOSO_3+2\frac{1}{2}\ CuHO$); Langite, ($CuOSO_3+3\ CuOH+H$); Cyanotrichite, ($SO_3,\ AlO_3CuO,\ H$); Woodwardite, ($CuOSO_3,\ CuOH,\ AlO_3H_3,\ 6\ H$); Aurichalcite, ($CuO,\ ZnO,\ CO_2,\ H$); A. Mysorin, ($CO_2,\ CuO\ FeO_3$); B. Lime Malachite, ($CO_2,\ CuO,\ SO_2,\ CaOFeO_3$); Chlorotile, ($Cu_3As_2O_8+6\ aq$); Cuprocalcite, ($(Cu_2O)_2\ CO_2+2\ CaCO_3+H_2O$); Chalcomenite, ($CuSeO_3+2\ aq$); Gerhardtite, ($4\ CuO,\ Na_2O_5,\ 3\ H_2O$); Guejarite, ($Cu_2S+2\ Sb_2S_3$); Horsfordite, ($Cu_{11}Sb_2$); Hydrocuprite, ($CuOH_2O$); Lautite, ($CuAsS$); Phillipite, ($CuOSO_3+Fe_2S_3O_{12}+aq$); Falkenhaynite, ($Cu_6Sb_2S_6$); Umangite, ($Cu_3Se_2$); Antlerite, ($3\ CuSO_4,\ 7\ Cu(OH)_2$).

Other Sources:

Copper matte, speiss, copper refinery slag, alloys from the smelting of other metals, residues and scrap metal.

Mining Localities:

United States, England, Australia, France, Canada, Chili, Peru, Portugal, Bolivia, Japan, Russia, Hungary, Siberia, Norway, North Wales, Ireland, Africa, Cuba, Fargo Islands, Spain, Germany, Islands of Timor and Timor-Laout and the adjacent islands of Polynesia.

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Production of Copper in the United States.[1]

(Smelter output, in pounds fine.)

In 1913, 1,224,484,098; 1914, 1,150,137,192; 1915, 1,388,009,527; 1916, 1,927,850,548; 1917, 1,890,000,000.

Commercial Metals:

Black Copper[2]—*Cu*, 99.400; *Ag*, .100; *S*, .3140; *Bi*, .1440; *Au*, .0008. Black Copper[3]—*Cu*, 99.170; *Bi*, .280; *Pb*, .123; *Sn*, *Sb*, *As*, .002; *S*, .244. Refined Copper[4]—

[1]*Production of Copper in the United States in* 1916. *Butler. U. S. Geol. Survey.*
[2]*Levol.*
[3]*Schwartz.*
[4]*Mining School at Fahlum.*

Cu, 99.460; *Fe*, .011; *Co* and *Ni*, .110; *Sn* and *Pb*, trace; *Ag*, .065; *Au*, .0015; *S*, .017. Mansfeld Refined[5]—*Cu* (by difference), 98.37; *Ag*, .02; *Ni*, .36; *Fe*, .05; *Pb*, .60; *O*, .58; *S*, .02. Mansfield Refined[5]—*Cu* (by difference), 99.48; *Ag*, .02; *Ni*, .32; *Fe*, .06; *Pb*, .12. Refined Tough Copper[6]—*Cu*, 99.94; *Fe*, trace; *Ag*, .056. Rosette Copper[7]—*Cu*, 98.48; *Pb*, trace; *Fe*, .75; *Ni*, .26; *Sb*, .60. Converter Anodes[8]*Cu*, 99.1300; *As*, .1183; *Sb*, .0534; *Ni*, .0420; *Co*, .0018; *Bi*, .0038; *Fe*, .0110; *Ag*, .1371; *Au*, .0008; *Se*, .0090; *Te*, .0170; *Pb*, .0065; *Zn*, .0035; *S*, .2610. Electrolytic Copper—*Cu*, 99.89000; *Sb*, .00515; *As*, .00108; *Ni*, .01000; *Ag*, .03360; *Bi*, none.

Qualitative Analysis:

Cupric Sulphate. ($CuSO_4+5\,H_2O$).

NH_4HO—greenish-blue precipitate. Soluble in excess to a clear blue solution of $(N_2H_6Cu)SO_4$. Color of solution destroyed by KCN.

$(NH_4)_2CO_3$—reaction similar to NH_4HO.

Na_2CO_3—greenish-blue precipitate of $CuCO_3.Cu(HO)_2$. Soluble in NH_4HO to a dark blue solution; soluble in KCN forming a colorless solution. $CuCO_3.Cu(HO)_2$ changes on boiling to black CuO; soluble in NH_4HO forming a blue solution.

KHO and $NaHO$—light blue precipitate of $Cu(HO)_2$; changes to CuO on boiling.

K_4FeCy_6—reddish-brown precipitate of Cu_2FeCy_6; insoluble in $HC_2H_3O_2$; decomposed by KHO forming a blue solution.

[5]*Dr. Steinbeck.*
[6]*Genth.*
[7]*Bodemann.*
[8]*Burns. "The Great Falls Electrolytic Refinery" Tran. A. I. M. E., Aug.*, 1913.

H_2S—black precipitate of CuS; soluble in HNO_3 and KCN; practically insoluble in hot Na_2S and K_2S solutions.

Yellow $(NH_4)_2S$ produces in cold slightly acid or neutral solutions, a deep orange precipitate of $Cu_2(NH_4)_2S_7$; completely soluble in excess, reprecipitated entirely as CuS when the solution is boiled thoroughly.

Place a platinum crucible lid in small beaker containing 10 or 15 *c. c.* of the solution of $CuSO_4$, place a little granulated *Zn* in contact with the *Pt*, add a few drops of *HCl* and metallic *Cu* will be deposited on the *Pt*.

Fe precipitates *Cu*, which is readily shown on a clean knife blade when it is dipped into an acidulated solution of *Cu*.

Dip a platinum wire in the solution of *Cu* and heat in a non-luminous flame; emerald-green tint, add a few drops of *HCl* to the solution and again moisten the wire with the solution and ignite, azure blue ending with an emerald-green color.

Uhlenhuth[1] mentions a new reaction for *Cu*. The reagent is prepared by dissolving .5 gram of 1, 2-diaminoanthraquinone-3-sulphonic acid in 500 *c. c.* of water and 40 *c. c.* *NaOH* solution (*d.* 1.38). An intense blue is produced by the formation of a complex salt; no other metal produces the same reaction. The color is distinct to 1.9 in 1 million, extreme limit 1.9 in 10 million.

Quantitative Analysis:

KCN Method. (*Ni* and *Zn* absent.)

Volumetric Method.—Place 1 gram of the finely divided alloy in 600 *c. c.* porcelain casserole. Add 10 *c. c.* of HNO_3(1.42), heat gently until the alloy is

[1]*Uhlenhuth. Chem.-Ztg.*, 34, 887.

thoroughly decomposed and evaporate to 5 *c. c.* Add 5 *c. c.* of HCl (1.20), boil five minutes, add 25 *c. c.* of water and 3 grams of $C_4H_6O_6$ and heat to dissolve. Neutralize with NH_4HO, add 10 *c. c.* in excess and dilute to 75 *c. c.* with water. Cool and titrate with standard KCN solution.

Before titrating, stand a second casserole containing the same volume of water beside the one containing the solution to be titrated. This will serve as a color comparison at the end point.

Standard KCN Solution.

Dissolve 35.8 grams KCN *c. p.* in 1 liter of water and standardize as follows: Place the selected weight of clean copper foil in 600 *c. c.* casserole and dissolve in 5 *c. c.* of HNO_3. Add 25 *c. c.* of water, neutralize with NH_4HO, add 10 *c. c.* in excess and dilute to 75 *c. c.* with water. Cool and titrate.

$$2\,Cu(NH_3)_4SO_4.H_2O+7\,KCN=$$
$$K_3NH_4Cu_2(CN)_6+NH_4CNO+2\,K_2SO_4+6\,NH_3+H_2O$$

$2\,Cu=7\,KCN$

$2\,Cu=63.57\times2=127.14$

$7\,KCN=65.11\times7=455.77$

$127.14:455.77=X:35.86.$ $X=10$ grams.

1000 *c. c.* KCN *V. S.* containing 35.86 grams. KCN

1000 *c. c.* KCN *V. S.* containing 35.86 grams $KCN=$ 10 grams Cu. (theoretical).

1 *c. c.* KCN *V. S.* containing .03586 gram $KCN=$ .01 gram Cu.

$$1\ c.\,c.\ KCN\ \text{solution}\ \frac{.0052\ \text{gram}\ Cu.}{1.70\ c.\,c.\ KCN}=.003059\ \text{gram.}\ Cu.$$

No. 2 Babbitt.

$$\frac{.003059^{1} \times 1.55\ c.c.\ KCN}{1\ \text{gram.}} \times 100 = .47\%\ Cu.$$

Mixture calculation=.50% *Cu*.

A standard solution of $CuSO_4 + 5\ H_2O$ can be used for standardizing the *KCN* solution and the weight of *Cu* taken for titration can be adjusted to correspond nearly to that of the unknown. This avoids error caused by titrating a small weight of *Cu* in the unknown and using a factor obtained by standardizing with much greater weight of *Cu*.

Dissolve 39.28 grams of $CuSO_4 + 5\ H_2O$ *c. p.* in 1000 *c. c.* of water and mix thoroughly.

1 *c. c.*=.01 gram *Cu* (theoretical) as
63.57 : 249.72=X : .03928. X=.01.

Take 25 *c. c.* of the solution with pipette, place in 250 *c. c.* beaker, add 2 *c. c.* of H_2SO_4, 4 *c. c.* of strong HNO_3 and dilute with water to 150 *c. c.* Connect platinum gauze cathode and electrolyze with a current ND_{100}=.5 ampere, 2.7 volts for fifteen hours. When the *Cu* is all deposited, which can be readily seen by testing 1 *c. c.* of the solution with H_2S, lower the beaker and at same time wash the cathode with distilled water maintaining the current meantime. Immerse the cathode in C_2H_6O for a few seconds, dry and weigh.

$$\frac{.2479\ \text{gram}\ Cu.}{25\ c.c.} = .009916\ \text{gram}\ Cu.$$

1 *c. c.* standard $CuSO_4 + 5\ H_2O$ solution=.009916 gram *Cu*.

[1]*Old solution.*

After the cathode has been washed with C_2H_6O, do not ignite and allow it to burn as it will cause a slight oxidation of the *Cu* thereby increasing the weight.

The *KCN* method will give satisfactory results with all weights of *Cu*, providing that all analysis is treated exactly in the same manner and the standardization of the *KCN* solution with about the same weight of *Cu* that is present in the unknown. In the standardization of a *KCN* solution, on the same day and in the same hour, with the same volume of HNO_3, NH_4HO and water, the *Cu* factors were:

$$(1)\ 1\ c.c.\ KCN\ sol. = \frac{.0052 \text{ gram } Cu.}{1.70\ c.c.\ KCN \text{ sol.}} = .003059 \text{ grm. } Cu.$$

$$(2)\ 1\ c.c.\ KCN\ sol. = \frac{.009916 \text{ gram } Cu.}{3.05\ c.c.\ KCN \text{ sol.}} = .003251 \text{ grm. } Cu.$$

$$(3)\ 1\ c.c.\ KCN\ sol. = \frac{.09916 \text{ gram. } Cu.}{28.80\ c.c.\ KCN \text{ sol.}} = .003443 \text{ grm. } Cu.$$

The above results show that the factors are not proportional to the weights of *Cu*.

Dickenson[1] has used a dilute solution of ammonical copper nitrate as a second solution. Should the assay be overrun, 5 *c. c.* of this solution is run in a flask, a little NH_4HO is added and the solution diluted with water to the same volume as the assay and titrated with the *KCN* solution. Should it take 4 *c. c.* of the *KCN* solution, 5 *c. c.* of the $Cu(NO_3)_2$ solution is added to the original assay and 4 *c. c.* deducted from the assay reading and the analysis finished as usual.

[1]*Eng. and Min. Jour., April* 25, 1914.

The solid KCN soon deteriorates after the container is once opened and the standard solution also becomes gradually weaker on standing, hence the solution should be standardized weekly with clean Cu foil *c. p.*, with standard $CuSO_4$ solution or with a babbitt of known Cu content.

Gravimetric Method.—Evaporate the filtrate from the $PbSO_4$ precipitate to about 100 *c. c.* (if Zn is present add 30% of its volume of HCl), heat to boiling and pass a rapid current of washed H_2S through the solution for fifteen minutes. Filter, wash with H_2S water and reserve filtrate and washings for the determination of Fe and Zn. Place the wet filter in a weighed platinum crucible and burn at a gentle heat in open crucible, until the filter is charred and the S is burned. Ignite strongly, cool and weigh as impure CuO. Dissolve the residue in crucible with a little HCl, transfer with a little water to a small beaker, filter and wash with hot water. Ignite filter and contents, cool, weigh, subtract weight from the total weight and multiply the difference by .7989 which will give the weight of Cu.

No. 2 Babbitt.

Weight of crucible$+CuO+SiO_2$=19.4961 grams.
" " " =19.4930 "

.0031 gram.

$$\frac{.0031\times.7989}{.5 \text{ gram.}}\times100=.49\%\ Cu.$$

The above method will give good results with small weights of CuO.

If the electric current is available, transfer the filtrate from the $PbSO_4$ to a 250 *c. c.* beaker and evaporate or dilute to 150 *c. c.* Add 4 *c. c.* HNO_3 (1.42) and electrolyze with a current of ND_{100}=.5 ampere. 2.7 volts for fifteen hours. Treat as in the electrolysis of Cu in standard $CuSO_4$ solution and reserve the solution from the Cu for Fe and Zn determination.

Estimation of traces Fe and Zn.

Boil the reserved filtrate from the H_2S precipitate (CuS) until free from H_2S, add 1 or 2 *c. c.* of HNO_3 and boil for a few minutes. Cool, render solution strongly alkaline with NH_4HO and allow to stand on hot plate about one hour. Filter on small ashless filter (reserve filtrate for Zn) and wash with hot water. Ignite, cool and weigh as Fe_2O_3. Multiply this weight by .7 which will give the weight of Fe.

No. 2 Babbitt.

Crucible+Fe_2O_3=19.2450 grams.
" =19.2434 "

.0016 gram.

$$\frac{.0016 \times .7}{.5 \text{ gram.}} \times 100 = .22\% \ Fe.$$

Acidulate the filtrate from the $Fe_2(HO)_6$ precipitate with $HC_2H_3O_2$, heat to about 80°C. and saturate with washed H_2S. Allow to settle, filter and wash with hot H_2S water. Dry filter and contents, ignite carefully in

weighed porcelain crucible, cool and weigh as *ZnO*. Multiply this weight by .80336 which will give the weight of *Zn*.

Analysis of No. 2 Babbitt.

Pb	69.37
Sb	17.85
Sn	11.91
Cu	.49
Fe	.22
	99.84

Sp. Gr. 9.6309

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CHAPTER V.

MISCELLANEOUS ANALYSIS.

According to Buchanan[1] the addition of a small amount of bismuth to babbitt, increases the anti-frictional properties of the alloy. The author has added .10% of bismuth to No. 1 Babbitt and the resulting alloy, has always been of a fine, close, even grain with remarkable wearing qualities.

Determination of Bismuth.

Gravimetric Method.—Place 1 gram of the finely divided alloy in a 400 *c.c.* beaker, add 15 *c.c.* of HCl and heat to dissolve. When action ceases, add a few drops of HNO_3 and boil gently until solution is complete. Add 40 *c.c.* of water, 4 grams of $C_4H_6O_6$ and heat to dissolve. Render solution strongly alkaline with $NaHO$ solution and heat nearly to boiling. Add 5 grams of Na_2S (dissolved in 50 *c.c.* of water), heat gently until the precipitate has settled, filter and wash precipitate thoroughly with 1% Na_2S solution. Wash the precipitate from the filter into original beaker with a little water, add HNO_3 and place beaker on hot plate. Place filter in small beaker, cover with 20% HNO_3 and boil gently until the paper is free from the precipitate and filter solution into main filtrate. Add sufficient HNO_3 to dissolve the remaining precipitate and evap-

[1] *Brassfounders' Alloys.*

orate the solution until yellow *S* appears, filter the solution into a 800 *c. c.* beaker and wash the filter with hot water. Dilute to 400 *c. c.* with water, place a small piece of litmus paper in the beaker, add NH_4HO until the acid is almost neutralized and finish with NH_4HO 1:3 until the solution is slightly cloudy and alkaline. Add 1 *c. c.* of *HCl* (1:3), dilute solution to 700 *c. c.* with water and allow to stand over night on warm plate. Filter, wash twice with hot water, dissolve precipitate on the filter with hot HNO_3 (1:4), and wash filter with hot water, allowing the solution and wash water to run into a 400 *c. c.* beaker. Neutralize as before with NH_4HO, add 1 *c. c.* of *HCl* (1:3) and allow to stand two hours at a gentle heat. Filter on weighed filter and wash thoroughly with hot water. Dry filter and contents in air bath at 100° C., for one hour and weigh as *BiOCl*. This weight multiplied by .80166 will give the weight of *Bi*.

No. 1 Babbitt.

Filter+*BiOCl*=23.2000 grams.
" =23.1987 "

.0013 gram.

$$\frac{.0013 \times .80166}{1 \text{ gram.}} \times 100 = .104\% \ Bi.$$

Mixture calculation=.10% *Bi*.

Colorimetric Method.—Place .5 gram of the finely divided alloy in 150 *c. c.* beaker, decompose with 10 *c. c.* of HNO_3 (1.42). Add 30 *c. c.* of water, boil, filter and wash with HNO_3 (1:3). Add NH_4HO and $(NH_4)_2CO_3$

to filtrate until solution is alkaline, stir thoroughly, filter and wash with dilute NH_4HO. Dissolve the precipitate on the filter with hot HNO_3 (1:3) and wash the filter with hot water. Add 10 *c. c.* of H_2SO_4 (1.84) to the solution and evaporate to SO_3 fumes. Cool, dilute with 50 *c. c.* of water and boil ten minutes ($BiSO_4$ is soluble, but not $PbSO_4$), filter into 500 *c. c.* marked flask, cool, dilute to the mark and mix. Place 100 *c. c.* in 100 *c. c.* Nessler jar, add 5 *c. c.* of 5% *KI* solution in water, mix and titrate blank with standard solution of *Bi* until the color matches that of the alloy.

Blank.

Place 100 *c. c.* of water in 100 *c. c.* jar, add 5 *c. c.* of 5% *KI* solution and 10 drops of H_2SO_4 (1.84).

Standard *Bi* Solution.

Dissolve .2 gram of pure *Bi* in dilute HNO_3, cool, add 10 *c. c.* of H_2SO_4 (1.84), and evaporate to SO_3 fumes. Cool, dissolve in water and dilute to 1000 *c. c.* 1 *c. c.*=.0002 gram of *Bi*.

No. 1 Babbitt.

$$\frac{.0002 \times .5 \text{ c.c.}}{.1 \text{ gram.}} \times 100 = .100\% \ Bi.$$

The addition of .10% metallic magnesium to No. 1 Babbitt forms a beautiful even close grained compact bearing metal. Its wearing qualities have been carefully noted by the metal mixer, on fast running motor bearings for over one year and it is said to give wearing qualities far surpassing that of any other alloy that has been used for the same purpose. As far as it is known, the author has been the first to use metallic magnesium

in babbitt. The alloy has not been patented and all are at liberty to use it.[1]

Determination of Magnesium.

Gravimetric Method.—Place 1 gram of the finely divided alloy in 250 *c. c.* beaker, add 10 *c. c.* of HNO_3 (1.42), cover, and heat gently until the fumes have disappeared. Add 10 *c. c.* of HCl (1.20), and heat gently until solution is complete. Add 10 *c. c.* of HCl (1.20), dilute with water to 100 *c. c.*, add NH_4HO in excess and 30 *c. c.* of strong Br water, heat to boiling, allow to settle, filter into 800 *c. c.* beaker and wash precipitate with hot water. Wash the precipitate from the filter into the original beaker with a little water, add 10 *c. c.* of HCl (1.20), heat to dissolve the precipitate, pour the solution over the filter and wash the filter with hot water. Add 30 *c. c.* of Br water to the solution, reprecipitate with NH_4HO, allow to settle, filter and wash with hot water. Add filtrate and wash water to first filtrate and for every 100 *c. c.* of solution, add 10 *c. c.* of HCl (1.20), stir thoroughly and pass a current of washed H_2S through the solution until it is saturated. Filter, wash precipitate with H_2S water, place the filtrate and wash water in porcelain casserole and evaporate to dryness. Ignite to volatilize the ammonium salts and the greater part of the $ZnCl_2$, if present. Cool, add 30 *c. c.* of

[1]*The metallic megnesium that was used for the experimental work was kindly donated by W. R. Seigle, Norton Laboratories, New York, N. Y.*

U. S., Patent. 933, 139, *Sept.* 7, 1910. *Enrique A. Touceda, Albany, N. Y. Antifriction alloy. Mg* 0.1–5%, *Cd* 10% *and Pb* 85–89.9%.

U. S., Patent. 934, 637, *Sept.* 21, 1910. *Enrique A. Touceda, Albany, N. Y. Antifriction alloy. Mg* 0.5–5% *and Cd* 95–99.5 *parts, with or without other metals.*

dilute HCl (1:10), heat to dissolve soluble salts, render slightly alkaline with NH_4HO, filter into 400 *c. c.* beaker and wash with hot water. Cool, add slowly, drop by drop, 10 to 15 *c. c.* of saturated filtered solution of $Na(NH_4)HPO_4$, stirring constantly, add one-third of its volume of NH_4HO (.90), and allow to stand in the cold overnight. Filter on small ashless filter and wash thoroughly with NH_4HO (1:3) reserving filtrate and wash water. Ignite precipitate, cool and weigh as impure $Mg_2P_2O_7$.

Crucible+impure $Mg_2P_2O_7$=19.2325 grams.
" =19.2280 "

.0045 gram.

Add 15 *c. c.* of water to the crucible and 10 to 20 drops of HCl, heat carefully to dissolve the soluble salt, filter, and wash with hot water. Ignite, cool and weigh as SiO_2. Subtract this weight from the first weight and reserve weight to combine with that recovered from the filtrate and wash water.

Crucible+SiO_2=19.2290 grams.
" =19.2280 "

.0010 gram. SiO_2.

.0045—.0010=.0035 gram $Mg_2P_2O_7$.

Evaporate reserved filtrate and wash water to dryness in platinum dish. Ignite carefully until the residue is white, add 20 *c. c.* of water and 15 to 20 drops of HCl, boil, filter into small beaker and wash with hot water. Render solution alkaline with NH_4HO, add 5 *c. c.* of

saturated filtered solution of $Na(NH_4)HPO_4$, stirring constantly, add one-third of its volume of NH_4HO (.90), stir thoroughly and allow to stand in the cold over night. Filter, wash with dilute NH_4HO (.96), ignite, cool and weigh as $Mg_2P_2O_7$. Combine this weight with the weight previously found and calculate Mg.

No. 1 Babbitt.

Crucible+$Mg_2P_2O_7$=19.2286 grams.
" =19.2279 "

.0007 gram.

.0035+.0007=.0042 gram $Mg_2P_2O_7$.

$$\frac{.0042 \times .21847}{1 \text{ gram.}} \times 100 = .0917\% \ Mg.$$

Mixture calculation=.10% Mg.

Qualitative Analysis of Babbitt.

Sn, Sb, Pb, Cu, Bi, Cd, Fe and *Zn.*

Place 2-5 grams of the finely divided alloy in 400 *c. c.* beaker, add cautiously 15 to 20 *c. c.* of HNO_3 (1.42) and heat gently until the alloy is decomposed. Evaporate to dryness, cool, add 5 *c. c.* of HNO_3 and 50 *c. c.* of water, boil five minutes, filter on double filter and wash once with hot water. The volume of the filtrate and wash water should be about 75 *c. c.*

Precipitate.

Place a portion of the precipitate in small beaker, add 5 *c. c.* of HCl and 10 *c. c.* of water, heat to boiling, add a few drops of HNO_3 and boil five minutes. Add 10

c. c. of water to the clear solution and several small bright iron nails, boil five minutes, filter (reserve filter and contents) and add $HgCl_2$ to filtrate; white precipitate$=Hg_2Cl_2=Sn$. as

$$SnCl_4+Fe=SnCl_2+FeCl_2 \text{ and}$$
$$2\ HgCl_2+SnCl_2=Hg_2Cl_2+SnCl_4$$

Wash filter and contents thoroughly with hot water, transfer the black precipitate from the filter to small beaker with a little water, add 5-10 *c. c.* of HCl and a few drops of HNO_3, boil, dilute with water and saturate solution with H_2S; orange precipitate$=Sb_2S_3$.

Filtrate.

Saturate with H_2S, filter, wash with hot water (reject wash water, reserve precipitate A) and boil filtrate free from H_2S. Add a few drops of HNO_3, boil, render solution strongly alkaline with NH_4HO; red precipitate $=Fe_2(HO)_6$. Filter, render filtrate acid with $HC_2H_3O_2$ and saturate solution with H_2S; white precipitate$=ZnS$.

Transfer reserved precipitate (A) to small beaker with a little water, add 5 to 10 *c. c.* of HNO_3 (1.42) and heat to dissolve the sulphides. Filter, add 5 *c. c.* of dilute H_2SO_4 (1 : 1) to the filtrate and allow to settle. Filter (reserve filtrate A), wash the white precipitate once with hot water, place filter and contents in original beaker, cover with NH_4HO (.90) and acidulate solution with $HC_2H_3O_2$. Heat to clear the solution and add $K_2Cr_2O_7$; yellow precipitate$=PbCrO_4$.

Render reserved filtrate (A) strongly alkaline with NH_4HO; blue solution$=Cu$. Filter (precipitate $B=Bi$ and filtrate $B=Cu$ and Cd), wash the precipitate free from Cu and dissolve on the filter with a little hot dilute HCl. Pour the solution into a large volume of water; white precipitate$=BiClO$.

Decolorize filtrate (*B*) with KCN and saturate solution with H_2S; yellow precipitate=CdS.

Miscellaneous.

Do not use borings from babbitt for analysis. Filings taken properly and mixed thoroughly, represent an average sample from the sample bar. Many chemists do not mention *Fe* that is found in babbitt in trifling amounts and in many cases, *Sn* is reported by difference.

If SnO_2 and Sb_2O_4 in HNO_3 solution is evaporated to dryness, taken up with HNO_3, diluted with water and filtered, *Sb* will be found in the filtrate. Hence the weighing of HNO_3 residues for the determination of total SnO_2 and Sb_2O_4 is mal-practice and the results most decidedly worthless.

The method of separation of *Sn* and *Sb* from traces of *Cu*, *Pb*, *Fe*, etc., by fusion with Na_2CO_3 and *S*, and the solution of the fusion in water, is valueless for daily routine work.

Place no faith in any method that advises the separation of *Pb* from much *Sn* and *Sb* by HNO_3 solution, as it is practically impossible to wash all the $Pb(NO_3)_2$ from the insoluble residue, and in the determination of *Pb* as $PbSO_4$, the ignition of a paper filter with particles of $PbSO_4$ adhering to it, require the most skillful treatment to avoid loss by oxidation and volatilization. For this reason the Gooch crucible is recommended.

The asbestos for the Gooch crucible should be treated for a few hours in each of the following acids: HCl, HNO_3 and H_2SO_4 (1:5), and allowed to remain in the latter solution until used. After placing the asbestos in the crucible, wash thoroughly with hot water, dry, ignite, cool and weigh. The crucible is now ready for use.

A modified Gooch crucible holder is sold under the name of "Esco"[1]. This is really a good article and avoids entirely the use of rubber tubing.

The *I* method for the determination of *Cu* will give accurate results with reasonable weights of *Cu*, but not always with small weights of the metal, unless the method is modified.

To insure the absence of *Zn* in large precipitates of *CuS*, 30% *HCl* by volume must be present.

Use the balance for the determination of specific gravity of alloys. Special hydrometers for taking the specific gravity of solids are not always trustworthy.

$$Sp.\ Gr. = \frac{W}{W - W^1}$$

W=weight of alloy in air.
W^1=weight of alloy in water.

Use weights from 40 to 50 grams of the alloy, duplicates will then check to the 3d., decimal place.

$$80\,R = 100\,C = 180\,F \text{ and } \frac{C}{100} = \frac{R}{80} = \frac{F-32}{212-32}$$

$$F\ 9/5\ C + 32 = 9/4\ R + 32$$
$$C\ 5/4\ R = 5/9\ (F-32)$$
$$R\ 4/5\ C = 4/9\ (F-32)$$

[1]*For sale by Eberbach and Son, Ann Harbor, Mich.*

Dr. Ure[1] gives the correct rule for computing the mean specific gravity of an alloy.

$$M=\frac{(W+w)\,Pp}{Pw+pW}$$

M=mean specific gravity of the alloy.
W and w=greater and least weights.
P and p=greater and least specific gravities.

When the calculated specific gravity of an alloy is less than the actual specific gravity, condensation has taken place (increase of specific gravity). When the specific gravity is lower than that calculated, expansion has taken place (decrease in specific gravity).

$$\frac{Wt.\ \text{per cent.}}{Sp.\ Gr.}=\text{Volume.}$$

$$\frac{At.\ Wt.}{Sp.\ Gr.}=\text{Atomic Volume.}$$

$$\frac{\text{Per cent.}}{\text{Molecular Weight.}}=\textbf{Molecular ratio or molecular proportion}$$

HCl dissolves *Sn, Fe, Al, Zn.*
HNO_3 " *Pb, Bi, Cd, As, Cu, Fe, Zn.* Oxidizes *Sn* and *Sb.*

Pb precipitates *Cu.*
Mg " *Fe, Zn,* etc.
Cu " *As, Sb, Hg, Au, Ag.*
Sn " *As, Sb, Hg, Au, Ag.*
Fe " *Cu, Sb, Bi, Au, Ag, Hg.*
Zn " *Sn, Sb, As, Cu, Pb, Hg, Bi, Co, Ni, Au, Ag.*

[1]*Ure's Dictionary. Vol. I, p.* 49.

	Spec. Grav.	Melting Point. (deg. C.)	Average Weight. (lb. per cu. ft)
Pb.	11.37 (a)	326.2 (f)	710.6
Cu.	8.89 (b)	1054. (g)	555.6
Sn.	7.294 (c)	232.7 (f)	455.8
Sb.	6.713 (c)	632. (h)	419.4
Fe.	7.8 (d)	1600. (*wrt.*) (i)	487.5
Zn.	6.9-7.2 (e)	433. (f)	440.6

Many metallurgists calculate the mean melting point of an alloy. This is considered unfair,[1] as many alloys have two melting points, the liquidus and the solidus points respectively.

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(a) *Matthiessen.*
(b) *Riche.*
(c) *Long.*
(d) *United States.*
(e) *Borchers.*
(f) *Person.*
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CHAPTER VI.

Babbitt Metal.

Notes on the Manufacture of Babbitt.

The following babbitts are usually all that is necessary for ordinary work. Each has given entire satisfaction when used for the purpose designated.

No. 1 Babbitt.

For motors and fast running machinery.

Sn	72.00
Pb	15.00
Sb	9.00
Cu	4.00
	100.00
Sp. Gr.	7.8

No. 2 Babbitt.

For slow running machinery.

Pb	69.50
Sb	18.00
Sn	12.00
Cu	.50
	100.00
Sp. Gr.	9.6

In preparing the babbitt, the following method was found to give the best results. Place the *Sn* and *Cu-Sn* alloy in hot pot and cover with fine coal dust. When the *Cu-Sn* alloy has melted, add the *Sb* slowly increasing the heat gradually until the *Sb* is entirely melted. Add the *Pb* in the same manner, which when melted will cool the alloy to about the pouring temperature, which should be as low as possible yet, fluid enough to mix thoroughly with iron paddle. The stirring must be continued during the entire pouring. By observing the specific gravity of the different metals that enter the alloy, it can be readily seen that the molten metal must be well mixed, otherwise there will be a segregation of the different metals. Many melters determine the pouring temperature by the ignition of a pine splinter when placed in contact with molten alloy.

The *Cu-Sn* alloy is made by melting together equal parts of *Cu* and *Sn*. This alloy is always kept in stock. By stirring the melted alloy thoroughly during the melting and pouring, and allowing the molten alloy to run into cold iron molds at as low a temperature as possible, segregation is entirely overcome. By covering the surface of the molten metal with about two inches of fine coal dust, the loss of metal by oxidation is almost trifling for the group of metals that form the mixture of the above babbitts. If there is a loss of over 1 per cent in the finished product, it can be traced invariably to waste, careless weighing or poor melting.

In one lot of 200 pounds of babbitt and using the Hauck Portable Kerosene Melting Furnace, No. 122, pot capacity 450 pounds, the finished babbitt was ready to pour in fifty minutes; burning three gallons of kerosene and with a loss of .63 per cent metal. This excellent work was due to the melter (J. Jette).

Fine coal dust for covering the molten metal is usually found on the tops of rafters in the blacksmith shop and the labor of grinding and sifting a hard or soft coal is avoided.

At one time not having molds, a length of railroad iron was used. This was turned on its side and the ends blocked with fire clay. When the clay was dry, it made an excellent mold.

One very important item is, not to assume that the crude commercial metals used in the manufacture of the alloy are chemically pure. The chemists report on an alloy will show at times, a gain or a deficit of certain metals. As a rule the crude metals can be relied upon to give results that are satisfactory.

Commercial Metals:

Cu.....	98.50%	—99.90%	(a)
Sn.....	93.50 "	—99.96 "	(b)
Sb.....	98.85 "	—99.85 "	(c)
Pb.....	99.87 "	—99.89 "	(c)

Examples of Calculations:

(1) The following metals are melted together: *Pb*, 50 lbs.; *Sn*, 25 lbs., and *Sb*, 15 lbs. The resulting ingot weighed 88.5 lbs. What is the percentage of metal lost?

$$50+25+15=90.0 \text{ lbs.}$$
$$\text{Ingot} \quad =88.5 \text{ "}$$
$$\text{Loss}= 1.5 \text{ "}$$
$$\frac{1.5\times100}{90}=1.66\%.$$

(a) *Sexton.*
(b) *Bruno Kerl.*
(c) *Min. and Sci. Press, July* 10, 1915.

(2) What is the percentage composition of the above mixture?

$$Pb \ldots\ldots \frac{50 \times 100}{90} = 55.55\%.$$

$$Sn \ldots\ldots \frac{25 \times 100}{90} = 27.78\text{ "}$$

$$Sb \ldots\ldots \frac{15 \times 100}{90} = 16.67\text{ "}$$

$$100.00\text{ "}$$

(3) Desire a bearing or casting of 150 lbs., of the above composition. What is the required weight of each metal?

$$Pb \ldots\ldots \frac{55.55 \times 150}{100} = 83.32 \text{ lbs.}$$

$$Sn \ldots\ldots \frac{27.78 \times 150}{100} = 41.68\text{ "}$$

$$Sb \ldots\ldots \frac{16.67 \times 150}{100} = 25.00\text{ "}$$

$$150.00\text{ "}$$

(4) What is the formula of the following alloy: *Cu*, 98.1%, and *Sn*, 1.90%?

$$\frac{98.1\%\ Cu}{63.57} = 1.5432$$

$$\frac{1.9\%\ Sn}{118.7} = .0160$$

$.016 : 1.5432 = 1 : X \qquad X = 96 \qquad SnCu_{96}$

(5) What is the percentage of each metal in the following alloy: $Sn_{25}Cu_5Sb_2$?

Sn.....	118.70×25=	2967.50
Cu.....	63.57× 5=	317.85
Sb.....	120.20× 2=	240.40
		3525.75

$$\frac{2967.50 \times 100}{3525.75} = 84.166\%\ Sn.$$

$$\frac{317.85 \times 100}{3525.75} = 9.015\%\ Cu.$$

$$\frac{240.40 \times 100}{3525.75} = 6.819\%\ Sb.$$

100.000%.

SAMPLING.

The following method for the sampling of babbitt, has given the best results and also entire satisfaction for a number of years:

Take the sample for analysis from the thoroughly mixed molten metal, just before the general pouring and cast in a cold iron mould of about the following dimensions, 4"×1½"×1". When the ingot is cold, the outside skin is removed with a file, thrown aside and filings are now taken by filing gently across the surface of the end of the ingot with a new clean file and, as for the contamination of the sample with particles of the file, it may be ignored safely in practice.

Do not take a sample from the ear or lug of a bar or casting as there may be, and is in many cases, a segregation of metal.

The analysis of No. 2 Babbitt represents a sample taken across the entire end of the sample bar.

The sample should be taken either by the chemist or by one who thoroughly understands the importance of the work, and the taking of samples by irresponsible boys, cheap labor and non-technical officials is certainly a stupid ridiculous practice, and if this mode of sampling is followed, the chemist will in many cases get the criticism.

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